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# PROPERTIES AND INTERACTIONS OF ORAL STRUCTURES AND RESTORATIVE MATERIALS

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U.S. DEPARTMENT OF COMMERCE  
Technology Administration  
National Institute of Standards  
and Technology  
Materials Science and Engineering Laboratory  
Polymers Division  
Dental and Medical Materials  
Gaithersburg, MD 20899

Prepared for:  
National Institute of Dental Research  
Bethesda, MD 20892

Annual Report for Period  
October 1, 1990 to September 30, 1991  
Issued May, 1992  
Interagency Agreement  
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U.S. DEPARTMENT OF COMMERCE  
Barbara Hackman Franklin, Secretary

TECHNOLOGY ADMINISTRATION  
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NATIONAL INSTITUTE OF STANDARDS  
AND TECHNOLOGY  
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The headings and subheadings of the annual report retain their designations from the original proposal. Since some sections of that proposal were deleted or reorganized into other sections, gaps appear in the numbering system for the annual report. The following sections from the original proposal were deleted or reorganized with the consequence that no technical report is given or required here:

PART I

- A.2 Lactone monomers
- A.5 Organometallic monomers
- A.6 Cyclic monomers
- A.8 Initiator systems
- B Filler systems
- C Interfacial bonding systems

PART II

Phases I-IV, and VI

PART III

- B.1 Bonded systems
- B.2 Diametral tensile strength
- B.3 Clinical performance
- C Superstrong prostheses



## Abstract of Research Plan

The research program described herein is designed to achieve a number of objectives leading to improved dental restorative materials, techniques and applications of dental materials science for improved delivery of health care. The bulk of the research is related in one manner or another to dental composites, cements, adhesives, and sealants. Composite research focuses on improvements through the development of more durable resin matrices, stronger and more durable coupling between fillers and resins, and defining the best overall combination of components, including curing systems, for improved performance of composites. This work has moved swiftly toward a major emphasis on the synthesis and applications of monomers which reduce polymerization shrinkage through the use of expanding monomers (or monomers which undergo much less shrinkage than conventional resin-matrix monomers).

Research on cements, adhesives and sealants employs many of the same methods as for composites but with further attention to adhesion to dentin and enamel. Analytical techniques include infrared (IR) spectroscopy, chromatography, x-ray analysis, nuclear magnetic resonance, hardness and tensile testing, and shrinkage dilatometry. A new effort involves a pilot study aimed at the use and further development of fluorescent dye spectroscopy for analysis of processes such as curing, applying coupling agents and monitoring the degradation of bonding between fillers and resin matrices; this application holds promise for far-reaching results.

Studies on the wear and durability of dental materials are conducted to complement the generic developmental work on composites, cements, adhesives and sealants. The wear work is to help guide further improvements in materials.

A second distinct area of effort focuses on dental alloy and ceramic systems. Weibull statistics and finite element stress analysis are employed for the determination of the strengths of ceramic and ceramic-metal systems as affected by processing parameters and thermo-mechanical properties.

This program is divided in Three Basic Parts for FY 1991; In FY's 92 and 93, Part II on Wear Resistance will be subsumed into Part I, Improvement of Dental Composites, Sealants, Cements and Adhesive Materials.

"The activity covered by this agreement consists of work which requires the definition of measurement methods, materials property data, and standards of basic scientific and engineering units, and the application of primary standards to insure equity and comparability in U.S. commerce, international trade, and technical activities. As such it complies with OMB Circular A-76, Revised under paragraph 5f ("Activities classified as Government responsibilities or are intimately related to the public interest")."

NO HUMAN SUBJECTS ARE INVOLVED IN THIS RESEARCH

PART I. - Improvement of Dental Composites, Sealants, Cements, and Adhesive Materials

The overall objective of Part I is to enhance the in vivo properties, especially durability and performance of resin-based and related dental materials (composites, sealants, adhesives, cements, etc.).

A. Improvement of Dental Resin Systems

The primary focus of Section A. of Part I is the development of new types of monomer systems that yield highly converted, stable polymers that have experienced slight or zero contraction or even a slight expansion on polymerization. In addition, monomers that are designed to enhance interfacial bonding within composites, and to tooth structure, will be synthesized.

This work will proceed as outlined:

A.1 Monomers which Polymerize with Expansion

Phase I:

Consists of several distinct, independent approaches primarily related to the synthesis of new monomers for double ring-opening polymerization.

Phase II:

Characterization of the new spiro monomers (e.g. IR, NMR), studies of their polymerization behavior and evaluation of polymer and copolymer properties will be performed.

Phase III:

The most promising spiro monomers will be used to formulate dental resin systems and composites which will be evaluated for polymerization shrinkage, mechanical strength, wear, water uptake, resistance to simulated oral fluids and adhesion potential.

#### A.4 Cyclopolymerizable Monomers

##### Phase I:

Consists of several distinct, independent approaches primarily related to the synthesis of cyclopolymerizable monomers and study of the cyclopolymerization process.

##### Phase II:

Characterization of the new monomers (e.g. IR, NMR), studies of their polymerization behavior and evaluation of polymer and copolymer properties will be performed.

##### Phase III:

The most promising new monomers will be used to formulate dental resin systems and composites which will be evaluated for polymerization shrinkage, mechanical strength, wear, water uptake, resistance to oral fluids and adhesion potential.

#### A.7 Synthesis, Characterization and Evaluation of Multifunctional Silane Agents

##### Phase I:

Evaluation of previously synthesized silane agent derived from BIS-GMA.

##### Phase II:

Multifunctional silane agents based on a polyfluorinated polyol (PFP).

##### Phase III:

Double ring-opening silanes.

- B. Improvement of Filler Systems for Composites and Cements
- D. New Resin Systems and Pretreatment Techniques for Bonding to Dentin

##### Phase I:

Pretreatments of dentin.

Phase II:

Synthesis, characterization and evaluation of new surface-active monomers based on  $\alpha$ -bromomethylacrylate.

Phase III:

Synthesis, characterization and evaluation of new PMDM type surface-active monomers

Phase IV:

Synthesis, characterization and evaluation of new surface-active monomers from trimellitic anhydride chloride.

Phase V:

Does not exist due to typographical error in original proposal.

Phase VI:

Synthesis, characterization and evaluation of fluorinated surface-active monomers.

Phase VII:

Synthesis, characterization and evaluation of the surface-active monomers based on N-t-butylaminoethylmethacrylate.

Phase VIII:

Investigate the self-curing mechanism of PMDM and amines.

E. Improvement of Dental Cements

The goal is to reduce their propensity to brittle failure and hydrolytic degradation, and enhance their biocompatibility and adhesion to tooth structure by changes in their structure and/or composition.

Phase I:

Develop new types of hybrid cement-composites based on polyelectrolyte cements plus water soluble monomers capable of cyclopolymerization.

Phase II:

Develop new types of hybrid cement-composites based on modified water soluble polymers.

Phase III:

Develop new calcium phosphate cements based on the apatite-forming reaction of dicalcium phosphate and tetracalcium phosphate using aqueous solutions of phytic acid or derivatives as the reaction media.

Phase IV:

Develop new polyelectrolyte cements from the cyclic polymers or copolymers of acrylic or methacrylic anhydride.

F. Fluorescent Probes for Assessing the Cure of Dental Composites and the Effectiveness and Durability of Coupling Agents. (A PILOT EXPLORATION TO DEMONSTRATE FUTURE APPLICABILITY IN DENTAL MATERIALS)

There are two primary objectives to this part of the proposal with one underlying common theme i.e., to improve properties of dental composite resins and resin-based cements by monitoring the degree of cure and the quality of the interfacial bond within composites through the application of NIST's fluorescent dye technology.

The first objective is to use cure-sensitive fluorescent dyes for making definitive measurements of the curing in composites and cements, thereby leading to improved resin formulations and initiator systems. It can be foreseen that this technology could also be useful for the American dental industry (research and product quality assurance) and might even find its way into the practicing dentist's office.

The second objective is to use fluorescent dyes for quantitative measurements of the effectiveness of various methods for applying a variety of coupling agents to filler substrates, and for determining the degradation resistance of the coupling agent-to-filler bond. This work can be extended to degradation of the interfacial bond between the resin matrix and the coupling agent-filler system. Here too, the potential application as a measurement technique in the clinical evaluation of composites, and the extension to use in dental practice, are reasonable possibilities.

The following work plan is envisioned:

## CURING TECHNOLOGY

### Phase I: (Pilot)

Develop dye systems which are physically and chemically compatible with dental monomers.

### Phase II: (Pilot)

Correlate fluorescent dye measurements with those from IR spectroscopy for quantitative assessment of degree of cure via fluorescence, (use neat resins, then composites and cements).

### Phase III:

(a) Use fiber waveguides for excitation of fluorescence in standardized forms of dental composite to determine: degree of cure and depth of cure as functions of the curing system (composite, initiator, method of initiation, etc.).

(b) Use the technique as research tool for developments in other sections of Part I of the proposal.

### Phase IV:

(a) Evaluate the degree of cure (in vitro) within simulated composite restorative fillings:  
(1) degree of cure.  
(2) depth of cure.

(b) Evaluate the cure of resin based cements under crowns, around inlays and with fixed partial dentures.

### Phase V:

Explore techniques, including hardwares, for applying the technology for use in the dental clinic for control of degree of cure and determination of depth of cure.

## COUPLING-AGENTS

### Phase I: (Pilot)

Use flat plates of composite filler material (quartz, fused silica, etc.) for evaluation of efficiency of attachment (by measurement of dye fluorescence):

- (1) technique variation.
- (2) coupling-agent chemistry.

Phase II:

For the most promising systems from Phase I, evaluate stability of attachment to plates:

- (1) water, various pH levels.
- (2) other food simulating liquids.

Phase III:

(a) Prepare dental composites with filler employing best coupling-agents from Phase II.

(b) Cure prepared composites between glass plates, mylar etc. to produce high degrees of cure. Then remove covering and expose composite to degradation environment.

(c) Debonding should yield a shift in the fluorescence color (wavelength). Upon successful demonstration of technique, use in other sections of Part I and promote for use by American industry.

Phase IV:

Using suitable filters, etc. conduct in vitro simulation of clinical examination of composite resin fillings exposed to wear in a degradation environment to determine potential use for:

- (1) clinical evaluation of composites.
- (2) diagnosis of failing composites in dental practice.

PART II. Wear Resistance and Durability Assessment of Dental Composite Restoratives and Related Materials

The general objective of this project is to develop a fundamental basis for enhancing the durability of dental composite restoratives and related materials. The approach is to define and delineate critical wear mechanisms applicable to the in vitro wear of these materials. For this work two classical pin and disc wear apparatuses will be employed: (1) a first generation unit, (I), which bathes specimens with flowing water and; (2) a second generation unit, (II), for which the bathing medium can be chosen from

a variety of food simulating liquids (including water) with the capability for providing constant exposure to the specimen. Various ancillary methods of degradative analyses will be employed. This project consists of the following phase:

Phase V: This phase has two components

A. Round-Robin Wear and Chemical Degradation Study of Posterior Composites

B. Complete Construction of the Modified Wear Testing Apparatus

### PART III. Dental Alloys, Ceramics, Metrology and Analyses

A. Stress in Prosthetic and Restorative Systems  
(Porcelain-Metal Thermo-mechanical Compatibility)

The objectives of this work are to make viscoelastic calculations of transient and residual stresses which develop in ceramic-metal systems as functions of processing, materials, and geometrical (dimensional) parameters.

Phase I:

For the viscoelastic models of porcelain and porcelain-metal slabs developed for ceramic-metal systems during the previous term of the interagency agreement: vary the coefficients of thermal expansion,  $\alpha_1$ ,  $\alpha_2$ ,  $\alpha_3$  of metal, opaque and body porcelains, respectively, to determine how stresses change at the porcelain body surface, body-opaque interface and opaque-metal interface. Each  $\alpha$  will be varied from a low to high value while holding the others constant. Other effects such as body, opaque and metal thicknesses, porcelain viscosities and activation energies will also be explored. Other geometry models such as shells or cylinders will be considered.

Phase II:

After one complete series of Phase I simulations at one cooling rate, several additional complete series will be run with the cooling rate as the variable.

Phase III:

Develop charts, figures and empirical formulae etc., useful for depiction of effects of  $\alpha$ 's, and cooling rates etc.

Phase IV:

For porcelain-metal systems, calculate stress relaxations at fixed temperatures or temperature ramps as functions of holding or cooling conditions. Vary the relative porcelain viscosities to determine trends which can be useful in design of more desirable stress-state systems.

Phase V:

For alloy systems which undergo phase transformations develop models which incorporate effects of phase transformations into viscoelastic calculations of stress as affected by such transformations under a variety of cooling regimens.

## PART I. Improvement of Dental Composites, Sealants, Cements and Adhesive Materials

### Overview

The quest for durable, esthetic, adhesive and biocompatible materials suitable for the restoration of lost tooth structure has long challenged dental materials researchers. A significant step toward the realization of this goal was the development of resin-based dental composites which overcame many of the shortcomings of the silicate cements (purely inorganic composites) and unfilled resin restoratives (purely organic composites based on methyl methacrylate and its polymers). The synthesis of BIS-GMA by Bowen, ushered in the modern era of resin-based dental composite restorative materials and also other resin-based dental materials. [1,2] The essential components of dental composites are: (1) a resin system comprising one or more vinyl monomers which on polymerization forms the matrix or continuous phase, (2) reinforcing fillers such as radiopaque glasses, quartz, minerals, ceramics, organic and hybrid organic-inorganic powders of various sizes, size distributions, and shapes form the dispersed phase, (3) an interfacial phase for bonding the continuous and dispersed phases, derived from vinyl silanes, titanates, zirconates, i.e., coupling agents, (4) a polymerization initiator system effective under ambient conditions, and (5) stabilizers for optimizing storage stability and also preserving the chemical stability of the hardened restoration. [3-25]

Unlike glass ionomer cements that bond to tooth structure, current resin-based composites are non-adhesive in nature. However, the acid-etch technique usually provides an effective micromechanical mechanism for bonding dental composites to enamel. [26,27] Bonding to dentin is a more challenging problem but recent developments have resulted in effective coupling agents for this substrate as well. [28-38] Efforts to enhance the durability and range of applications (e.g., posterior as well as anterior fillings) of dental composites include: optimization of the types, sizes, shapes and volume of the dispersed phase, reductions in the solubility parameter, residual vinyl unsaturation, and polymerization shrinkage of the resin phase and the development of more effective interfacial bonding phases. [39-70]

Dental sealants have similar compositions and chemistry but are unfilled or only lightly filled and usually contain a higher proportion of diluent monomer(s). Resin-based systems also are widely used in other applications (e.g., adhesives, core build-up and crown and bridge materials, laminating veneers, impression, denture and maxillofacial

materials.

Dental cements, which also have a composite nature, find use in a wide variety of dental applications. In restorative dentistry they are employed as temporary, intermediate, and (in the case of glass ionomer cements) permanent filling materials. Their chemistry of hardening involves a series of acid-base reactions involving ion-exchanges that result in the development of a matrix into which are imbedded partially reacted basic filler particles. An ion-exchange mechanism involving polyelectrolyte cements (e.g., glass ionomer) and mineralized tissue also may explain their adhesion to tooth structure. [71-83]

Two types of dental cements can be distinguished depending on their water content: (1) those that are aqueous based (e.g., zinc phosphate, polycarboxylate, glass ionomer) in which water plays a role both in their setting and in the development of their molecular and micro structures, and (2) those that are relatively non-aqueous in nature, although catalytic amounts of water or other polar compounds (e.g., acetic acid) are needed to activate the acid-base reactions and to achieve clinically acceptable setting times for (e.g., ZOE, EBA, hexyl vanillate-EBA, dimer acid, etc.)

Basically this section is divided into three areas of research:

Improvement of Dental Resin Systems for Composites and Sealants.

(Synthesis, Characterization, Formulation and Evaluation)

Bonding of New Resin Systems to Tooth Structure.

(Synthesis, Characterization, Formulation and Evaluation)

Improvement of Dental Cements.

(Synthesis, Characterization, Formulation and Evaluation)

**A. Improvement of Dental Resin Systems for Composites and Sealants**

**Objective**

The goal of this research task is to enhance the durability of dental composite, sealant, cement and adhesive materials through the use of low-shrinking, but highly thermosetting and stable resins.

**A.1. Monomers which Polymerize with Expansion**

**Background**

Polymerization shrinkage of dental resins is widely regarded as one of the most serious limitations of these materials. The stresses resulting from the contraction of the organic phase of composites can result in microcracks, filler debonding and marginal gap formation. [39-56] Elaborate layering methods for composite placement [55,56] and time consuming multi-step bonding protocols [52] have failed to provide a composite-dentin interface which can reliably withstand the contractile forces and remain intact. The resulting gap formation at either the surface margin or the cavity base can promote staining and/or secondary caries formation, both of which can necessitate replacement of the restoration. The residual polymerization stresses and shrinkage-related defects may also be at least partially responsible for the less than satisfactory durability and wear performance noted for many commercial composite materials. [62,64]

The goals of this research project have been the synthesis and evaluation of monomers capable of double ring-opening polymerization with an expansion in volume. Free radical polymerizable, asymmetric spiro orthocarbonate monomers have been selected as monomers which can accomplish the stated goal. [48] These compounds can be utilized as comonomers in polymerizations with common methacrylate dental monomers to provide resin systems with minimal or no polymerization shrinkage and increased adhesion potential. [45,48]

#### **PROGRESS REPORT**

During this reporting period, progress in Phase I (monomer synthesis) was made in the following areas:

- a) Formulation of previously synthesized spiro monomers in dental resins.
- b) Synthesis of modified ring-opening monomers.
- c) Synthesis of styrene-like spiro monomers.
- d) Synthesis of 2-methylene spiro monomers.
- e) Synthesis of 2,3-bis(methylene) spiro monomers.

No work was conducted on sections f) through j) of Phase I. The progress results from Phase II (characterization and polymerization of new monomers) and Phase III (formulation and evaluation of experimental resins) which pertain to the individual sections of Phase I are included here to simplify the reporting of results.

- a) Formulation of previously synthesized spiro monomers in

dental resins.

The dimethyl- and phenyl-substituted spiro monomers 1 and 2, respectively, were incorporated into dental resins with ethoxylated bisphenol A dimethacrylate (EBPADM) and compared with control resins consisting of either EBPADM alone or EBPADM and 1,6-hexanediol dimethacrylate (HDDM). The monomers, which are both liquids at room temperature, easily mixed into the EBPADM to provide resins with viscosities intermediate to those of the two control formulations. Composite pastes were prepared at a powder liquid ratio of 4 to 1. The composites were cured using a variety of polymerization techniques (Table 1). The diametral tensile

Table 1  
Diametral Tensile Strength of Dental Composites

Composition of Resin	Weight %	DTS, MPa $\pm$ sd <sup>a</sup>	Initiation Method
EBPADM	100	49.4 $\pm$ 2.3 (6)	photo-cure
"	"	44.4 $\pm$ 2.1 (6)	dual-cure
EBPADM/HDDM	65.2/34.8	46.0 $\pm$ 3.3 (5)	photo-cure
"	"	45.1 $\pm$ 4.6 (5)	dual-cure
EBPADM / 1	71.9/28.1	34.9 $\pm$ 1.7 (6)	photo-cure
"	"	40.6 $\pm$ 0.8 (6)	evacuated/ photo-cure
"	"	47.4 $\pm$ 1.7 (6)	dual-cure
"	"	47.8 $\pm$ 1.0 (6)	chemical-cure
EBPADM / 2	68.4/31.6	50.4 $\pm$ 2.8 (6)	dual-cure

<sup>a</sup> Numbers in parentheses indicate the number of samples.

strength results indicate that the spiro monomers are most efficiently copolymerized with the dimethacrylate comonomer when the chemical or dual cure procedures are utilized. In these examples, there was no decrease in the mechanical strength of the experimental materials compared with the controls. This is a significant improvement over the performance of prior, less reactive spiro monomers [43, 44] which did not have the exocyclic double bond situated directly adjacent to one of the spiro oxygens. It is not understood why the spiro monomer component in the composite materials appears reluctant to polymerize under photo cure conditions. A refractive index mismatch between the monomers and the glass filler was ruled out as the cause.

b) Modified ring-opening monomers.

In our continuing study to understand and exploit double ring opening monomers to control polymerization shrinkage, a wide variety of spiro orthocarbonate monomers have been investigated. The asymmetric synthesis technique utilized permits a range of ring sizes and substituents [48] which in turn can influence the mode of polymerization and the properties of the resulting polymers. However, previous attempts to prepare functionalized spiro orthocarbonates suitable for subsequent derivatization were unsuccessful. A procedure has now been devised (Scheme 1) which accomplishes the synthesis of a hydroxyl-functionalized spiro monomer. The new monomer 3 contains an exocyclic double bond on the spiro group for free radical ring opening. The liquid monomer may be polymerized at this stage to produce a hydroxyl-modified polycarbonate. This monomer is significantly more polar than other alkyl or aryl-substituted spiro orthocarbonates and this property may be advantageous for monomer infiltration at the dentinal surface.

The hydroxyl substituent also gives access to a number of derivatives which can expand the potential applications of the ring opening monomers. To date, the simple conversion of the hydroxyl group to a methacrylate has been achieved (Scheme 2). The difunctional monomer 4 can engage in 1,2-vinyl addition polymerization through the methacrylate functionality and independent ring opening polymerization via the remote exocyclic double bond. The result is highly crosslinked bulk polymers (Scheme 3) which display varying amounts of ring opening depending on polymerization conditions. It appears that lower temperature polymerizations or exposure to air during polymerization are conditions which favor the ring opening. Dilute solution polymerization of 4 yielded a small amount of soluble polymer in which the conversion of the methacrylate double bond and the spiro-vinyl group were approximately equal. The solution polymerization technique appears to achieve nearly quantitative ring opening.

Resin formulations incorporating monomer 4 and ethoxylated bisphenol A dimethacrylate (26.6 : 73.4 by wt.) were prepared and evaluated. Conversion of the different double bonds of the reactive groups could be analyzed and compared by infrared spectroscopy. The photo cured unfilled resin gave 77 and 53% conversions for the methacrylate and spiro groups, respectively.

c) Styrene-like spiro monomers.

In an effort to synthesize ring-opening monomers with free radical polymerization reactivities comparable to

conventional methacrylate dental monomers, the use of "styrene-like" spiro orthocarbonates has been explored. A relatively simple route utilizing a vinyl-substituted cyclic thionocarbonate precursor (5; Scheme 4) was proposed as means of synthesizing such a monomer (6; path A). A wide variety of thionocarbonates have been used in a similar manner to prepare asymmetric spiro orthocarbonate monomers with different ring sizes and substituents. [48] However, in the attempted conversion of intermediate 5 to the corresponding monomer 6, an alternate reaction pathway (B) predominated which resulted in the formation of dimer 7 which does not appear useful. A "styrene-like" ring-opening monomer such as 6 is of interest since it addresses many of the concerns associated with these types of monomers. It should have good reactivity towards free radical addition due to the aromatic stabilization of the resulting radical intermediate. It could, in theory, favor ring opening since the disubstituted radical would be hindered from direct 1,2-addition, thereby effectively increasing the intramolecular ring-opening isomerization pathway. Finally, "styrene-like" monomers would yield ortho-phenylene polycarbonates which should provide for somewhat higher modulus and greater solvent resistance than similar non-aromatic ring-opened polymers.

In retrospect, the difficulties associated with the attempted synthesis of monomer 6 appear to result from the presence of an easily isomerizable vinylidene group directly adjacent to the reaction site, and from the different nature of the oxygens in the intermediate (phenolic versus benzylic). Several possible reaction sequences which should alleviate these problems can be envisioned. One such pathway, shown in Scheme 5, is currently being pursued.

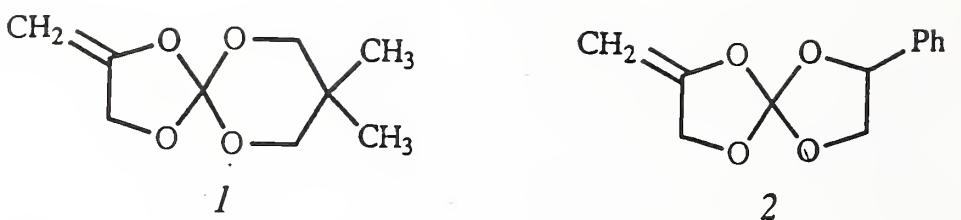
d) 2-Methylene spiro monomers.

Our experience with a variety of free radical polymerizable spiro monomers has indicated that the 2-methylene spiro orthocarbonates, with the exocyclic vinyl group adjacent to one of the spiro-fused oxygens, provide relatively good reactivities and ring-opening efficiencies. In order to directly compare the effect of substituents on the polymerization of these monomers, compounds 8 and 9 were prepared. This offered an opportunity to observe the influence of aliphatic versus aromatic substituents in position to stabilize the resulting radical formed on ring opening. The expectation was that the phenyl substituents would favor the ring-opening process by virtue of the lower energy benzylic radical which could be generated. In polymerization studies, however, the diphenyl monomer 9 yielded only slightly more ring-opened polycarbonate segments than the dimethyl-substituted monomer 8. There were

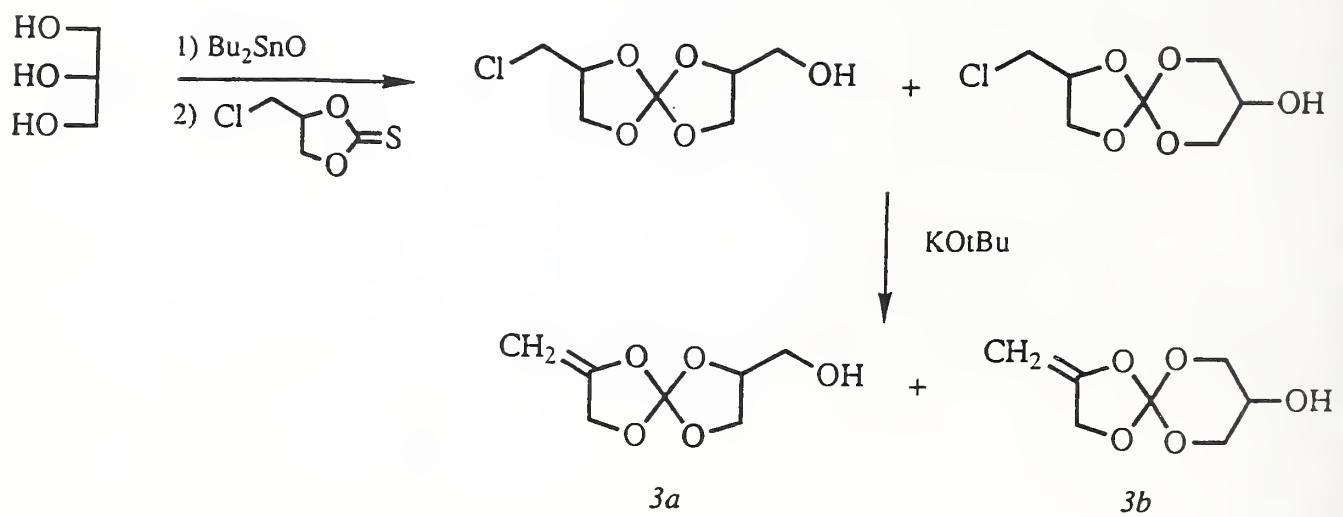
significant differences in the properties of the two polymers with the diphenyl providing a higher softening temperature and somewhat greater solvent resistance.

e) 2,3-Bis(methylene) spiro monomers.

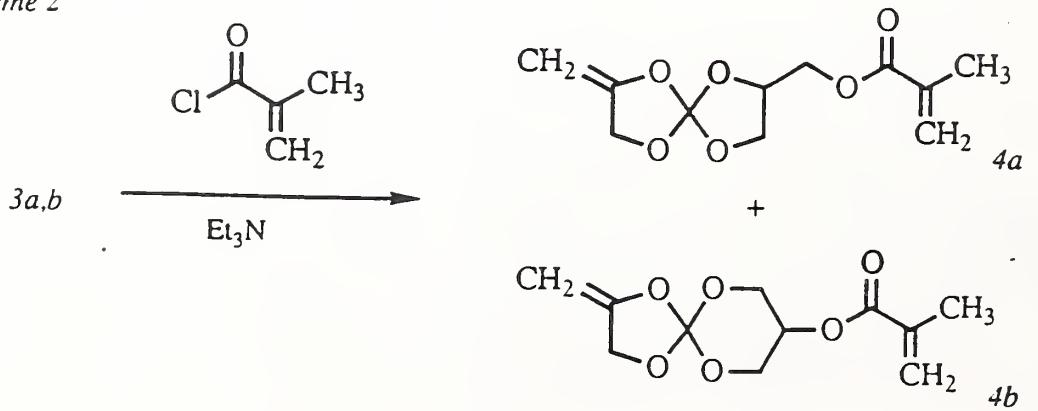
Another approach taken to improve the free radical polymerization reactivity and to introduce crosslinking potential in ring opening monomers has centered on 2,3-bis(methylene) spiro compounds. The highly reactive spiro monomers 10 and 11 were prepared and studied under a variety of polymerization conditions. The excellent radical reactivity can be attributed to the conjugated 1,3-diene group. The monomers offer highly crosslinked polymers in near quantitative conversion from bulk homopolymerizations. Brittle, glassy polymers were rapidly formed under chemical or photo cure conditions even at ambient polymerization conditions. However, when either of the bis(methylene) monomers were formulated with BIS-GMA or ethoxylated bisphenol A dimethacrylate comonomers, the attempted photo or dual cure polymerization of the resins was unsuccessful. Even prolonged irradiation failed to significantly harden the resin. Upon standing in the dark, the resin gradually gelled. This behavior indicates the formation of a complex between the methacrylate and bis(methylene) vinyl groups. Therefore, applications involving the 2,3-bis(methylene) spiro monomers may be limited to homopolymerizations, such as with coatings, or to copolymerizations with other less reactive ring-opening monomers.



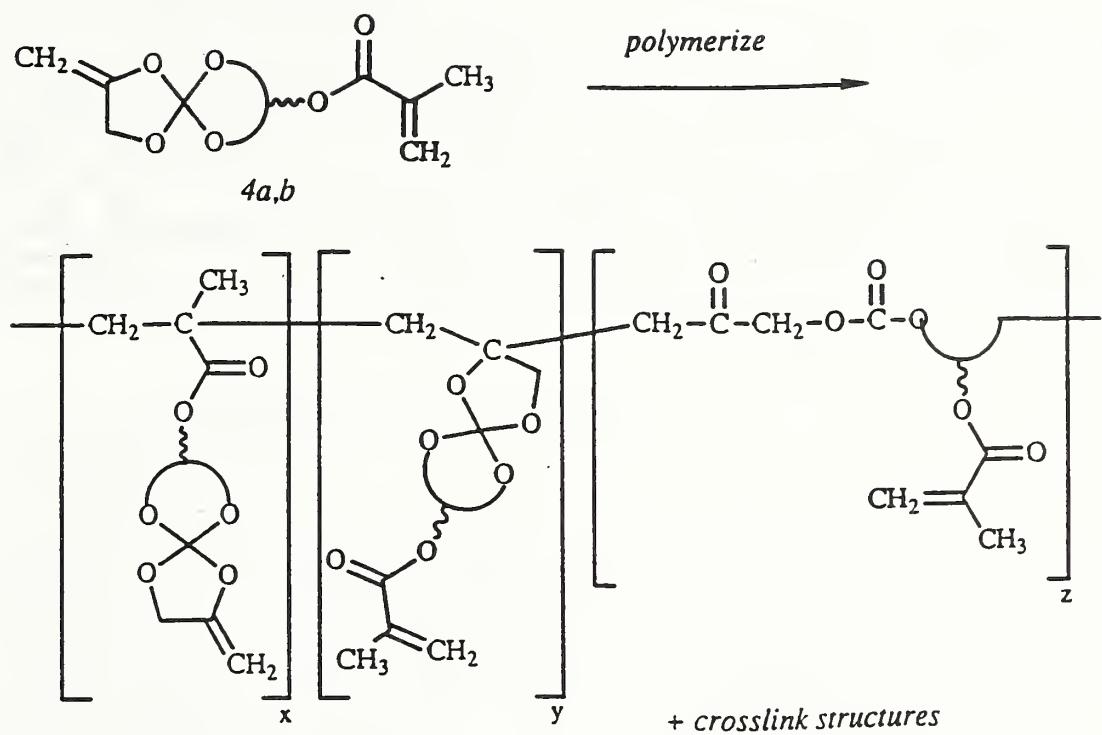
*Scheme 1*



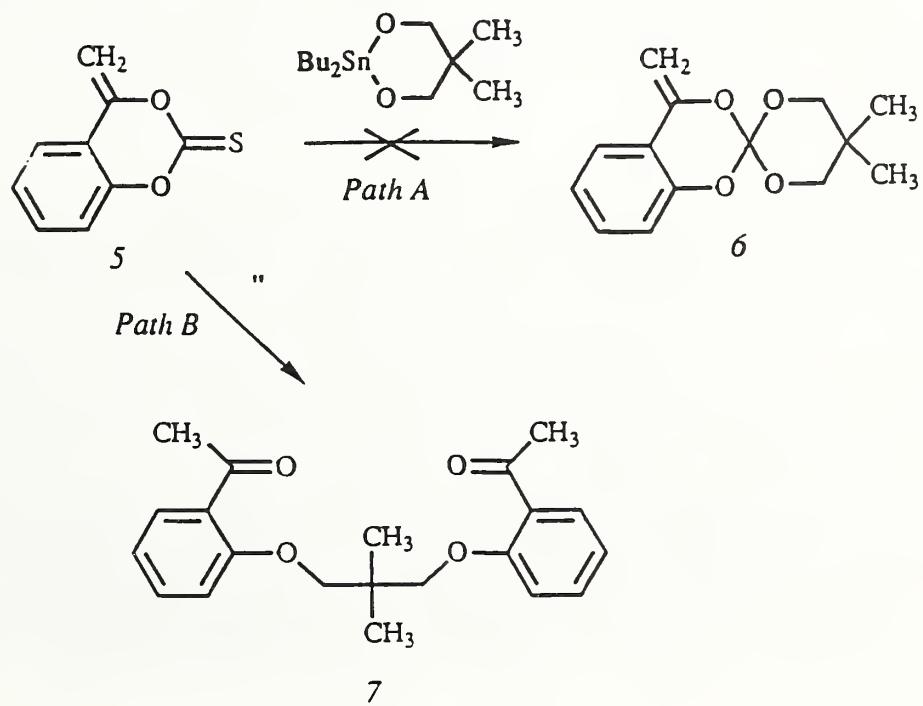
*Scheme 2*



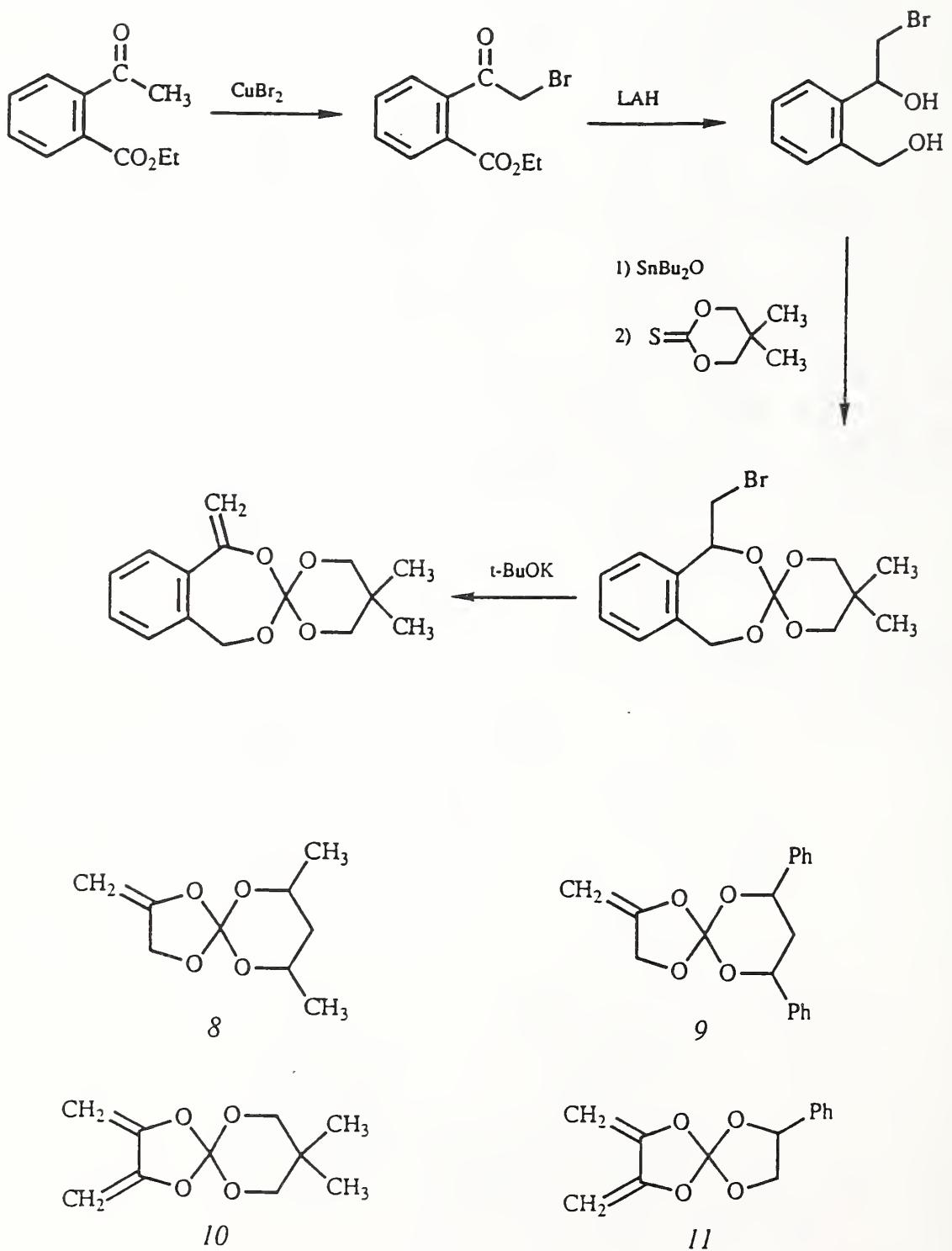
Scheme 3



Scheme 4



Scheme 5



### A.2. Lactone Monomers

No work was performed using the highly reactive  $\alpha$ -methylene lactone monomers in dental resins. A paper summarizing our prior findings on this subject was prepared and submitted for publication.

### A.3. Low Surface Energy Monomers

(Relevant portions of this originally proposed section are now incorporated into section A.4, part d).

### A.4. Cyclopolymerizable Monomers

#### Background

The serendipitous discovery that the DABCO-catalyzed reaction of an acrylate ester and formaldehyde would proceed beyond the initial  $\alpha$ -hydroxymethyl acrylate intermediate (1; Scheme 1) to a 1,6-diene 2 has uncovered a rich vein of new monomers. [84,85] The monomers are essentially ether-fused dimethacrylates with the ester groups located externally. This ester functionality can be varied to significantly alter the properties of the monomers and their corresponding polymers. [86] The 1,6-diene configuration in the monomer gives access to an intramolecular cyclization pathway for polymerization. Depending on the polymerization conditions, linear polymer can be formed exclusively via cyclopolymerization, or crosslinked polymer can be obtained by a combination of the 1,6-cycloaddition and 1,2-addition polymerization modes (Scheme 2).

In addition to the difunctional 1,6-diene monomers, multifunctional oligomers capable of several discrete cyclopolymerizations per chain, thereby yielding highly crosslinked polymers, have been synthesized and evaluated. [87] All these new monomers share several properties that make them attractive prospects for use in dental resins. [88] By virtue of the cyclopolymerization process, high degrees of conversion can be achieved while yielding relatively high modulus polymeric materials. An efficient cyclopolymerization process also offers a route to significantly reduced levels of polymerization shrinkage compared with conventional dimethacrylate polymerizations. The goals of our work in this area are to extend and establish the bounds in this new avenue of chemistry and to evaluate these novel cyclopolymerizable monomers in dental resin applications.

## PROGRESS REPORT

During this reporting period, progress in Phase I (monomer synthesis) was made in the following areas:

- d) Synthesis of fluorinated 1,6-dienes.
- e) Studies of the aldehyde insertion reaction.
- f) Synthesis of monomers via intramolecular aldehyde insertion.
- i) Synthesis of water soluble monomers.

### d) Synthesis of fluorinated 1,6-dienes.

The combination of hydrocarbon acrylate esters with paraformaldehyde in the presence of DABCO yields the cyclopolymerizable 1,6-diene as the main product. Depending on the ester functionality, the reaction can also produce a 1,4-diene condensation product in concentrations ranging from 0 to approximately 15%. The 1,4-diene configuration in this product would require that a high energy four-membered ring form if cyclopolymerization were to take place through a head-to-tail intramolecular addition, thereby discounting this polymerization pathway. The use of fluorinated acrylate esters in the aldehyde insertion reaction was found to result in predominantly 1,4-diene products due to the electronegativity of the ester group. [89] We have had success in preparing fluorinated 1,6-dienes if an acrylate with  $R = -CH_2CH_2CF_3$  is employed; however, these types of fluorinated acrylates or alcohols are extremely scarce. Therefore, in an attempt to prepare 1,6-dienes from readily available fluorinated starting materials, the diacrylate of hexafluorobisphenol A was synthesized and subjected to the standard aldehyde insertion reaction conditions (Scheme 3). The result was a nonviscous multifunctional oligomer 3 which had internal diene linkages in a 2.1 to 1 ratio favoring the 1,4- over the 1,6-diene. The oligomer had an average of approximately five repeat units per oligomer chain. This type of fluorinated oligomer would be expected to provide a highly crosslinked, hydrophobic matrix; however, it would not be expected to offer the low degree of polymerization shrinkage due to inefficient cyclopolymerization.

### e) Studies of the aldehyde insertion reaction.

The aldehyde insertion reaction has been exploited to convert a variety of acrylate starting materials into 1,6-diene monomers capable of cyclopolymerization. The use of paraformaldehyde can give high yields of these monomers

while the substitution of formalin, a 37% aqueous formaldehyde solution, as the aldehyde substrate yields the  $\alpha$ -hydroxymethyl acrylate as the principal reaction product. [90,91] The scope of the aldehyde insertion reaction was broadened to include substituted aldehyde starting materials. The effect of the substituents on monomer synthesis (Scheme 4) and subsequent polymerization was investigated with acetaldehyde ( $R = \text{methyl}$ ) and benzaldehyde ( $R = \text{phenyl}$ ). The results are shown in Table 1. The formation of the  $\beta,\beta$ -disubstituted products 4a and 4b

Table 1  
Synthesis and Polymerization<sup>a</sup> of  $\beta,\beta$ -Disubstituted Methacrylate Monomers

Monomer	Monomer Synthesis Yield, %	Homopolymerization polymer yield, %		Copolymerization with MMA, 1:1 bulk	
		bulk	solution	yield polym	monomer 4 in co- polymer, %
4a, $R = \text{CH}_3$	77	7	4	67	36
4b, $R = \text{Ph}$	53	0	0	34	13

<sup>a</sup> All polymerizations were conducted at 65°C with 1 wt% AIBN as initiator.

was relatively efficient; however, unlike the analogous reaction with the less hindered formaldehyde substrate, no 1,6-diene condensation products were observed. Apparently steric effects induced by the additional  $\beta$ -substituent preclude further reaction. An attempt was made to prepare the asymmetric 1,6-diene by combining the hydroxy acrylate 4a and its unsubstituted counterpart 1 in the presence of the DABCO condensation catalyst (Scheme 5). As a practical benefit, this procedure would offer an avenue to multifunctional cyclopolymerizable monomers if a dialdehyde substrate were employed. However, the steric repulsion of even the single  $\beta$ -methyl substituent was enough to block the formation of the asymmetric diene 5 and instead, only the symmetrical unsubstituted monomer 2 was obtained.

Studies with the liquid monomers 4a and 4b (Table 1) indicate that the polymerizability was severely compromised by the presence of the two  $\beta$ -substituents. The decreased reactivity can be correlated with increasing steric bulk of the  $\beta$ -substituent. Conversely, the  $\alpha$ -hydroxymethyl acrylate monomer ( $R = H$ ) undergoes rapid, high yield polymerization. [90,91] Monomers 4a and 4b both engaged in copolymerization with methyl methacrylate, but again, the lower degree of incorporation of the bulkier phenyl-substituted monomer into the copolymer demonstrates its lower relative reactivity.

In another investigation involving the aldehyde insertion reaction, the catalyst which accomplishes the conversion was varied and the effect of this change on reaction rate and product distribution was determined (Table 2). While all the amines (except triethylamine) evaluated as catalysts were

Table 2  
Effect of Catalyst on Aldehyde Insertion/Condensation Reaction

Catalyst <sup>b</sup>	Product Distribution <sup>a</sup>			
	Unreacted acrylate, %	1,6-Diene, %	$\alpha$ -Hydroxy-methyl, %	Other products, %
TEA	99 <sup>+</sup>	trace	0	0
QN	2	64	29	5 <sup>c</sup>
DABCO	6	60	27	7 <sup>d</sup>
DBU	98	1	trace	0
HMTA	99	trace	0	0
TPP	71	17	12	0
TBP	59	trace	trace	40 <sup>c</sup>
BDPPE	79	11	10	0

<sup>a</sup> Product distribution after 17 h at 65°C.

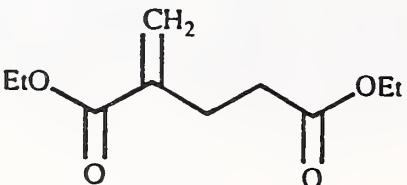
<sup>b</sup> TEA= triethylamine; QN= quinuclidine; DABCO= 1,4-diazabicyclo[2.2.2]octane; DBU= 1,8-diazabicyclo[5.4.0]undec-7-ene;

HMTA= hexamethylenetetramine; TPP= triphenylphosphine; TBP= tri-n-butylphosphine; BDPPE= bis-1,2(diphenylphosphino)ethane.

<sup>c</sup> Mainly 1,4-diene product.

<sup>d</sup> Mainly 1,8-diene product.

<sup>e</sup> Dimer of ethyl acrylate with the following structure:



heterocyclics with the ligands from the nitrogen tied-back in rings, only DABCO and quinuclidine functioned as suitable catalysts for the 1,6-diene formation. Aromatic phosphine derivatives can also accomplish the conversion to the desired product but the aliphatic phosphine yields an alternate, monofunctional acrylate dimer product exclusively with virtually no formaldehyde participation.

f) Synthesis of monomers via intramolecular aldehyde insertion.

An attempt to synthesize the hydroxy-substituted  $\alpha$ -methylene lactone described in the proposal was unsuccessful. The necessary aldehyde-acrylate precursor (6; Scheme 6) was readily prepared from salicylaldehyde and acryloyl chloride. Upon treatment with DABCO, intermediate 6 was not converted to the desired methylene lactone 7, but rather, underwent a reduction to the benzylic alcohol 8.

In an analogous reaction an aliphatic aldehyde-substituted acrylate (9; Scheme 7) was successfully converted to the cyclic product 10. There was no evidence to indicate that the reaction proceeded through the condensation to yield a 1,6-diene type product.

i) Synthesis of water soluble monomers.

Since the ester groups can be varied in the cyclopolymerizable monomers, the functionality can be tailored to fit specific application needs. We were interested in preparing cyclopolymerizable monomers which would be water soluble or water compatible for use as crosslinkable modifying agents for hybrid cement composites and polymeric calcium-phosphate cements as described in Part I.E. (phase I) of the proposal. One approach to this problem involved the use of tetrahydrofurfuryl acrylate in the aldehyde insertion reaction. While the difunctional product 11 (Scheme 8) was significantly more polar in nature than other cyclopolymerizable monomers prepared previously, it was not water soluble. It may still prove to be useful as an adhesion promoting bonding agent. The  $\alpha$ -hydroxymethyl intermediate 12 was also isolated from the reaction mixture and this product was quite water soluble though not able to cyclopolymerize.

Alternatively, we sought to synthesize a cyclopolymerizable, difunctional HEMA derivative. Direct attempts to use 2-hydroxyethyl acrylate in the aldehyde insertion reaction were unsuccessful due to complications attributed to the hydroxyl group. Therefore, the alcohol was first protected as the tetrahydropyranyl derivative (13; Scheme 9) and then converted to the 1,6-diene product. The blocking group was

then removed to yield the hydroxyethyl terminated 1,6-diene monomer 15. Like its monofunctional HEMA analog, the cyclopolymerizable monomer was completely water soluble. The monomer was polymerized to a crosslinked glassy polymer which swells in water but not in dichloromethane. Aqueous solutions of the monomer can also be polymerized to produce hydrophilic gels.

In Phase III work on formulation and evaluation of dental resins based on cyclopolymerizable monomers, the *in situ* synthesis and formulation of an all cyclopolymerizable monomer system comprised of multifunctional oligomer and difunctional 1,6-diene monomer was investigated. Varying compositions of ethyl acrylate and ethoxylated bisphenol A diacrylate (EBPADA) were combined with paraformaldehyde and DABCO and heated at 95°C for 18 h. The crude reaction product was then passed through a small silica gel pad to remove the DABCO. The filtrate was then warmed under high vacuum to remove any unreacted ethyl acrylate. The residue was then visible light activated with camphorquinone and ethyl 4-dimethylamino benzoate to complete the cyclopolymerizable resin formulation.

The resins were comprised of the simple difunctional monomer 2 (Scheme 10) and a series of extended multifunctional monomers/oligomers such as 16. As shown in Table 3, the ethyl

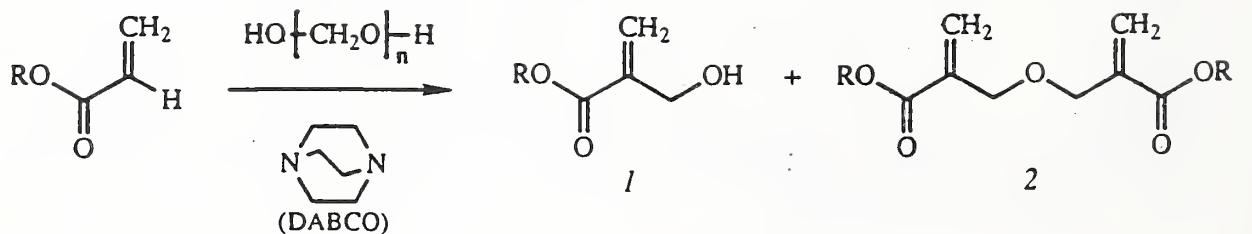
Table 3  
Characterization and Evaluation of *In-situ* Formulated Cyclopolymerizable Resins

	Resin		
	#1	#2	#3
<u>Reaction composition<sup>a</sup></u>			
EA	2	2.5	3
EBPADA	1	1	1
PF	3	3.5	4
DABCO	0.3	0.35	0.4
<u>Resin composition</u>			
incorporation of EA/EBPADA	1.17	1.71	1.92
EA in 2 / EA in 16	1.05	1.19	1.52
Diametral Tensile Strength photocured composite P/L=4, MPa	45.4 ± 1.6	-	43.4 ± 1.8

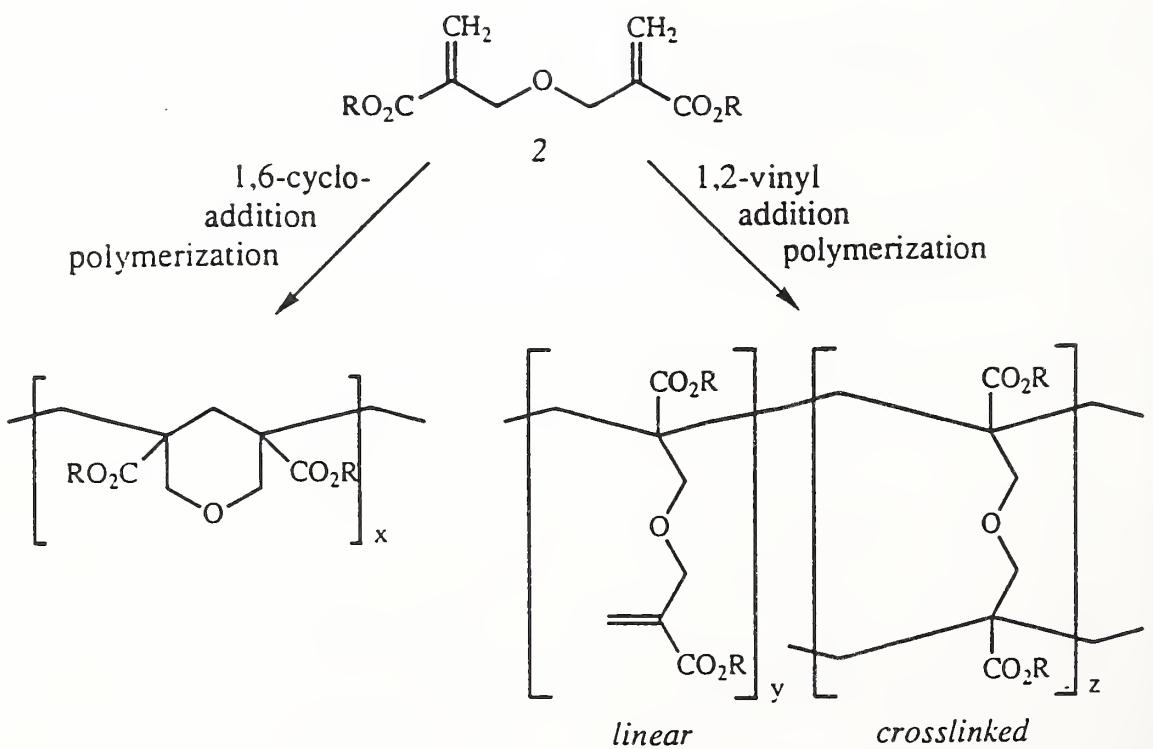
\* EA= ethyl acrylate; EBPADA=ethoxylated bisphenol A diacrylate; PF= paraformaldehyde; DABCO=1,4-diazabicyclo[2.2.2]octane.

acrylate to EBPADA ratio ranged from 2 (resin #1) to 3 (resin #3). This variation resulted in resins with differing compositions and properties. For example, the resin #3 had a significantly lower viscosity than resin #1 due to the greater amount of monomer 2 present to serve as diluent. A study of the degree of conversion of the photo cured unfilled resins has been completed but the results remain to be calculated. The diametral tensile strength results shown for the photo cured composites demonstrate that these materials possess adequate physical properties. An evaluation of the polymerization shrinkage of these cyclopolymerizable resins will also be conducted.

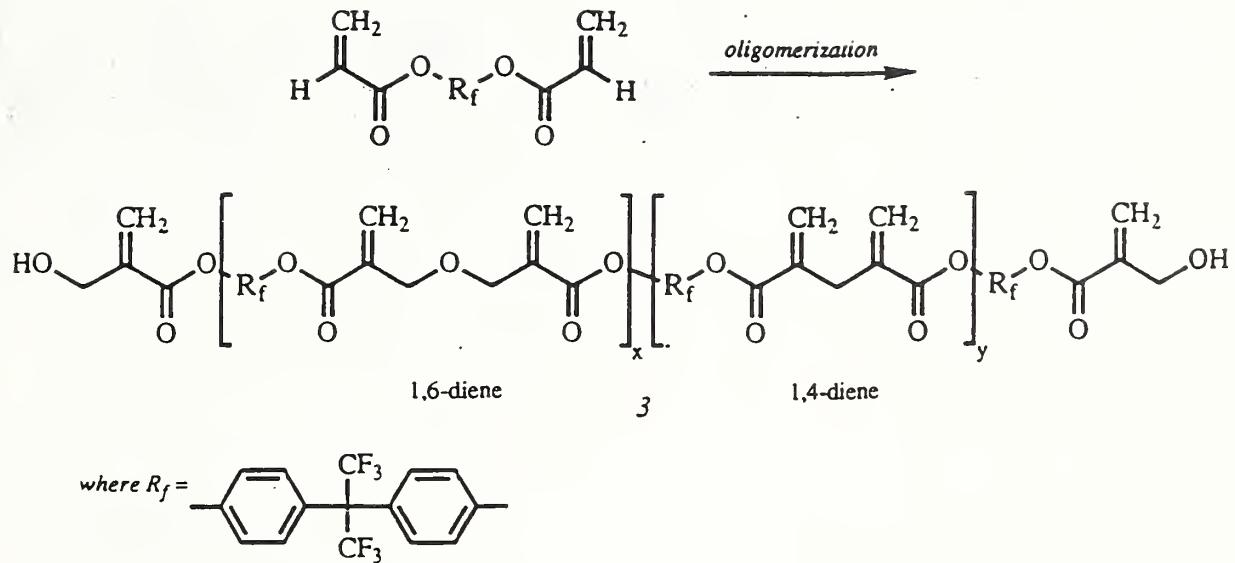
*Scheme 1*



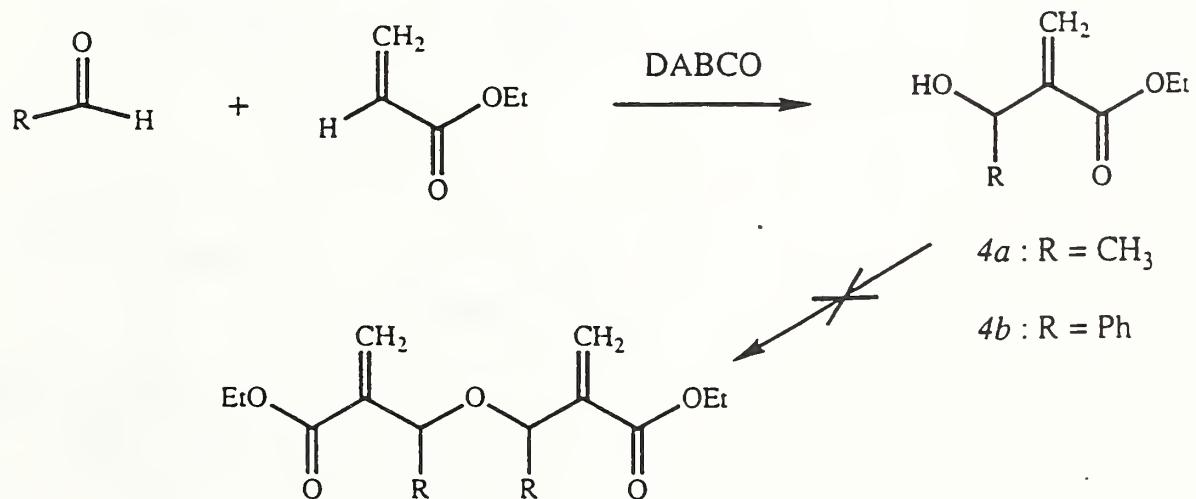
*Scheme 2*



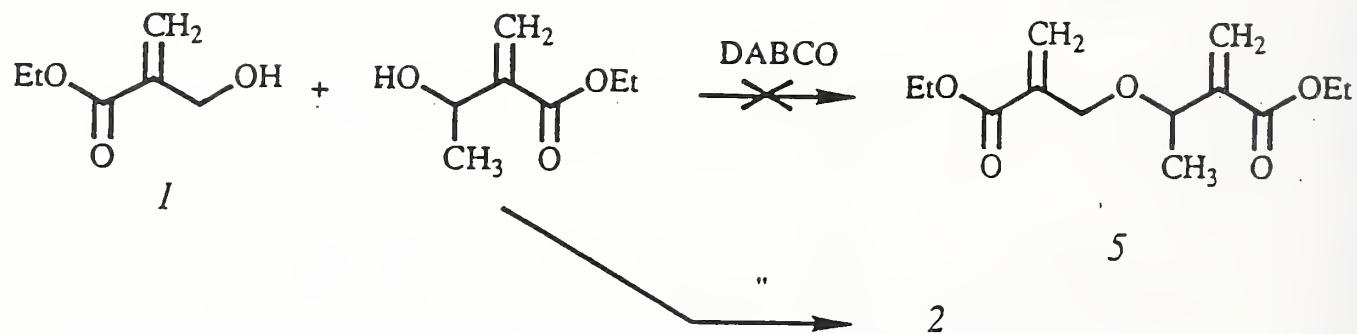
Scheme 3



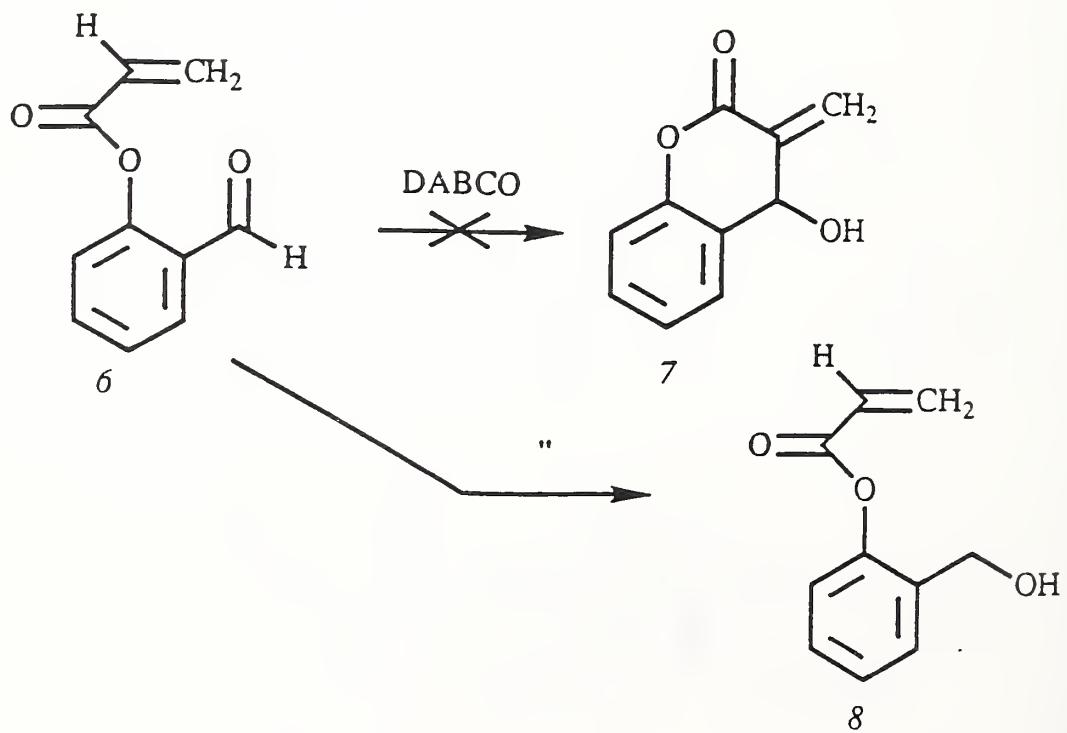
Scheme 4



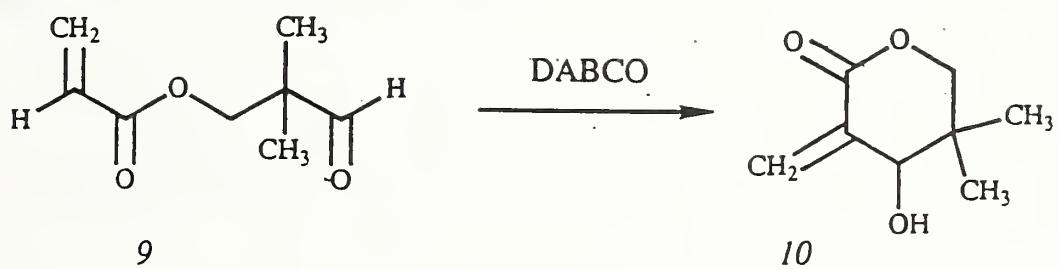
Scheme 5



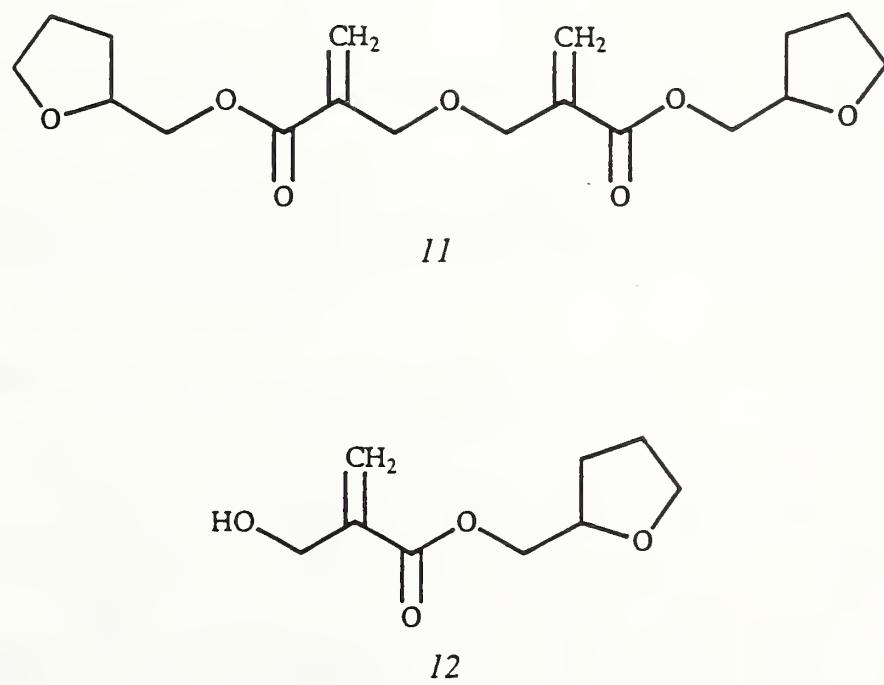
Scheme 6



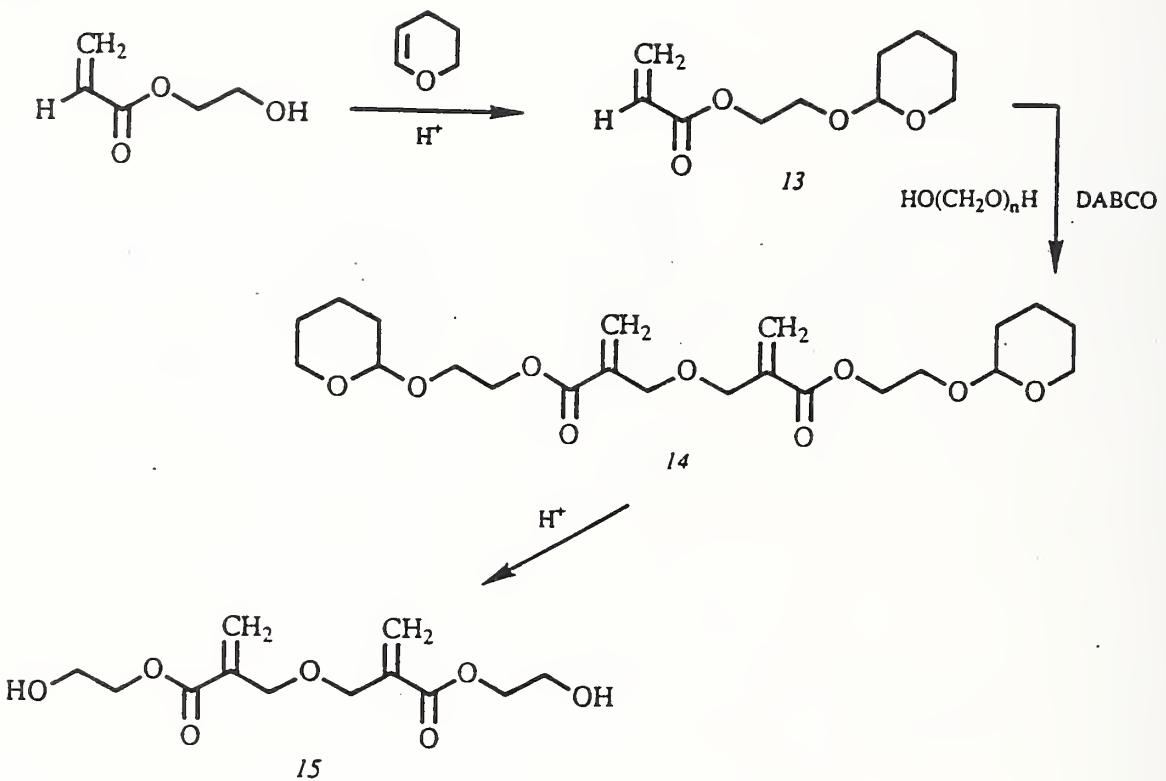
*Scheme 7*



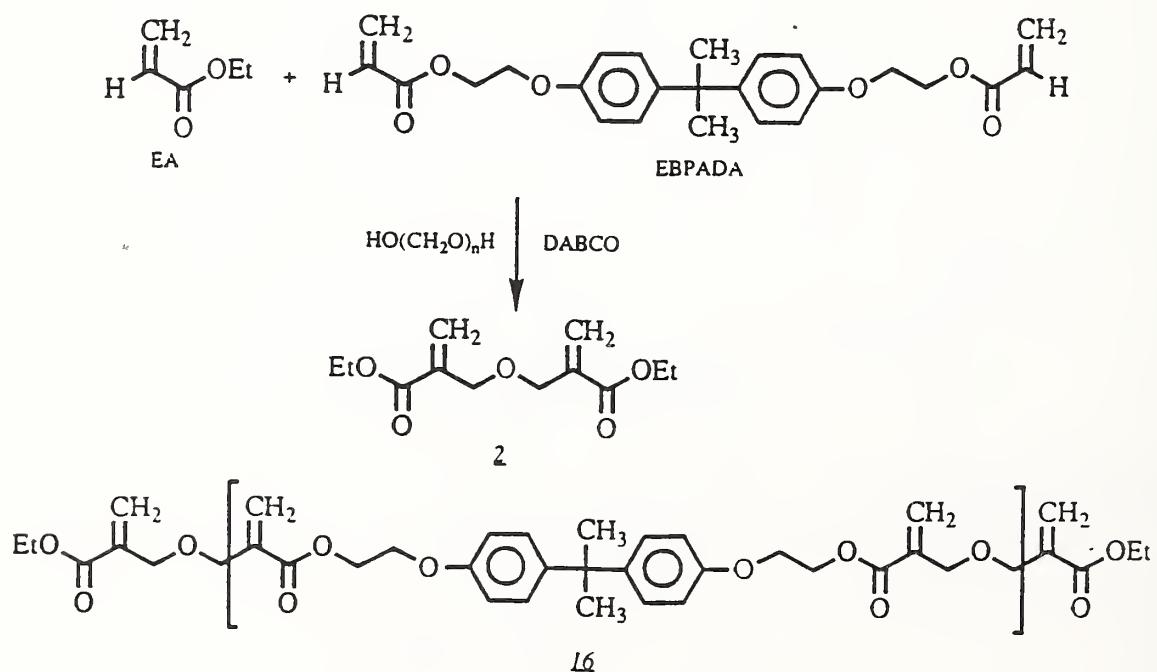
*Scheme 8*



Scheme 9



Scheme 10



A.7 Synthesis, Characterization and Evaluation of Multifunctional Silane Agents

Background

The weakest link in silane treated siliceous composites is the oxane bond that forms between the silane agent and the silanol groups on the filler surface. The oxane bond that forms between the coupling agent (e.g. A-174) and the mineral phase is vulnerable to hydrolysis, especially if it is not completely formed [92]. The extent of copolymerization of the resin system with the coupling agent also is an important factor in determining the durability of the interphase as is the nature of the filler, its size, surface area, topography, shape, etc. The objective of this section is to develop coupling agents and methods of surface modification that will improve the quality of the interfacial bonding phase in composites and thereby enhance their durability.

An ancillary part of this study is to develop methods suitable for the evaluation of the efficacy of the silane coupling agent and the silanization technique. (see section F.)

**PROGRESS REPORT**

**Phase I**

Evaluation of a previously synthesized silane agent derived from BIS-GMA.

The multifunctional silane coupling agent derived from BIS-GMA and 3-isocyanatopropyltriethoxysilane [93,94] unfortunately polymerized on storage and a new batch will have to be prepared. An evaluation of this multifunctional silane agent will be reported in Phase II.

During this Phase I period we had the privilege of having Dr. Kikuchi of Nihon University as a guest scientist whose interest was in silanization and mechanical methods for evaluating their efficacy. We decided it would be useful to this project to avail ourselves of his special expertise in this area. Consequently, we are collaborating on several projects that are designed to elucidate the quality of interfacial bonding in resin based dental materials. One such project involves a comparison of the diametral tensile strength and the uniaxial tensile strength as a method for assessing the effects of coupling agents in composites [95-99].

There exists some concern about the suitability of the diametral compression test as a method for determining the tensile strength of resin based dental composites. Previous studies with commercial dental composites using both macro-

and microfilled materials indicate that the uniaxial tensile strength (UTS) and the diametral tensile strength (DTS) values can be similar or divergent depending on the nature of the reinforcing phase [96,99].

In this study several well characterized, highly filled composites were prepared using two mixtures of 2,2-bis-[p(2'-hydroxy-3'-methacryloxypropoxyphenyl)]propane (BIS-GMA) and triethyleneglycol dimethacrylate (TEGDMA) as the monomer system with either a macro- or a microsized particulate glass filler. Composite specimens were prepared using both silanized (3-methacryloxypropyltrimethoxy silane) and unsilanized glass fillers. Specimens were polymerized by visible light activation using camphorquinone (CQ) and ethyl 4-dimethylaminobenzoate (4EDMAB) as the photooxidant and photoreductant, respectively. Specimens of the photocured unfilled resins also were prepared. All specimens were stored at 37°C in distilled water for one day. The results are summarized in the following table and Figures 1-4.

#### COMPARISON OF DTS AND UTS OF DENTAL RESINS AND COMPOSITES

RESIN COMPOSITION* (wt/wt)	REINFORCEMENT (wt%)	TENSILE STRENGTH IN MPa (STD. DEV)	
		UTS	DTS
BIS-GMA/TEGDMA (1/1)	SILANIZED MACROFILLER <sup>+</sup> (83.3)	86(4)	51(5)
	UNSIANIZED MACROFILLER (83.3)	23(2)	25(1)
	SILANIZED MICROFILLER <sup>++</sup> (57.7)	46(9)	43(15)
	UNSIANIZED MICROFILLER (50.7)	41(4)	26(3)
	NONE (0)	62(5)	26(1)
BIS-GMA/TEGDMA (7/3)	SILANIZED MACROFILLER <sup>+</sup> (83.3)	78(2)	53(1)
	UNSIANIZED MACROFILLER (83.3)	23(4)	27(2)
	SILANIZED MICROFILLER <sup>++</sup> (59.5)	35(4)	35(2)
	UNSIANIZED MICROFILLER (52.9)	27(2)	18(2)
	NONE (0)	69(4)	30(2)

\*Activated with 0.2 wt% CQ and 0.8 wt% 4EDMAB; <sup>+</sup>silanized with 0.5% w/w 3-methacryloxypropyltrimethoxysilane; <sup>++</sup>silanized with 7.5% w/w of the silane agent (silanization procedure described in reference 94).

Thus, in the case of the silanized macrofilled composites and the unfilled BIS-GMA/TEGDMA polymers UTS is significantly greater than DTS. By contrast, for the silanized microfilled composites UTS and DTS are virtually the same. With unsilanized macrofiller UTS and DTS are virtually the same. The results also show that for macrofilled composites, UTS is a more sensitive indicator than DTS to the effects of the coupling agent. Contrary to the results with macrofilled composites, DTS rather than UTS seems to be the more sensitive indicator of the efficacy of

the silane coupling agent in the case of microfilled composites. Generally, the difference between the silanized and unsilanized versions of microfilled composites are much less than in the case of macrofilled composites. These results indicate that in evaluating the efficacy of silane coupling agents by mechanical test methods it is important to consider not only the test method but also the type and state of subdivision of the glass used as the dispersed phase.

Fig.1 UTS and DTS values of macrofilled composites  
Bis-GMA/TEGDMA:1/1

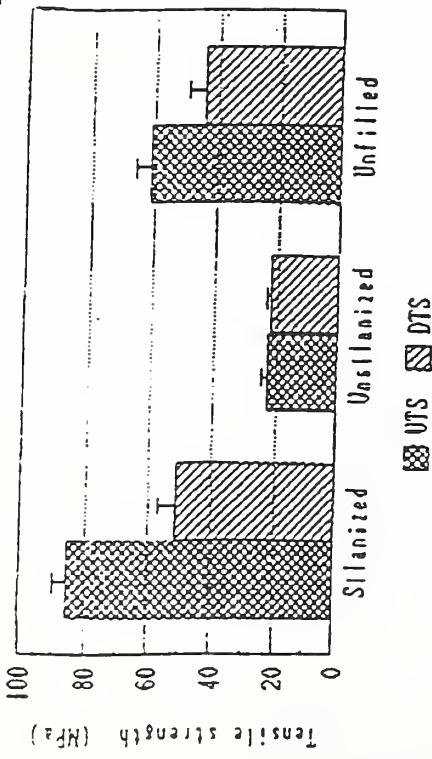


Fig.3 UTS and DTS values of microfilled composites  
Bis-GMA/TEGDMA:1/1

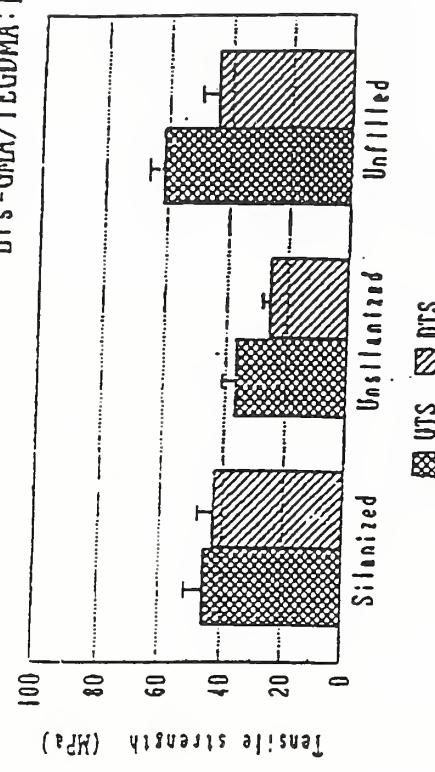
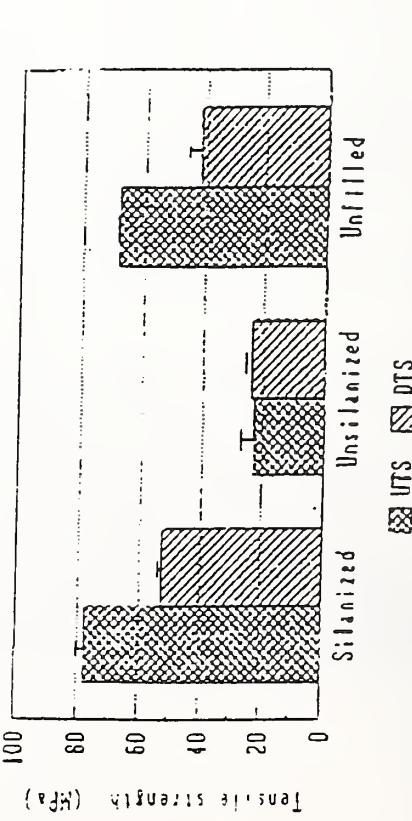


Fig.4 UTS and DTS values of microfilled composites  
Bis-GMA/TEGDMA:7/3



## B. Improvement of Filler Systems for Composites and Cements

### PROGRESS REPORT

#### Background

Considerable effort has been given to improving the properties (especially wear resistance and polishability) of dental composites through modification of their filler systems. In addition to a wide variety of macrofilled and microfilled composites, submicron macrofilled, hybrid filled and megafilled inserts composites have been developed. There also has been a trend toward somewhat softer fillers that would not abrade opposing enamel or accelerate the wear process. Modifications in the surface porosity of fillers as a means of enhancing interfacial bonding and wear resistance is another significant development.

The basic approach of this proposal is to optimize the properties of composites by controlling the type, size, shape, distribution and volume percent of the dispersed phase. In addition to the traditional siliceous fillers (radiopaque glasses, fused quartz, silicates, mica, microfine silicas) emphasis is given to other softer, more ductile filler types such as various phosphates, metaphosphates, polymers, etc. as candidates for use in the filler phase of these materials.

Although Section B is no longer a part of our proposal it is necessary to consider the effects of different types of fillers, size effects, etc. on the silanization process which is an integral part of Section A.7. Therefore, some parts of Section B relating to how filler characteristics affect the degree and durability of silanization are now incorporated into Section A.7.

## D. New Resin Systems and Pretreatment Techniques for Bonding to Dentin

#### Background

Current dental composites, in contrast to polycarboxylate and glass ionomer cements, are not inherently adhesive to enamel or dentin. The discovery of the acid etch pretreatment technique by Buonocore, however, provided an effective means of bonding composites to enamel. [26,27]

The generation of surface microporosities in enamel by acid treatments involving both inorganic ( $H_3PO_4$ ,  $HNO_3$ ) and organic acids (citric, pyruvic) permits infiltration of the resin into this substrate which by polymerization then forms a

micromechanical, interlocking, tag-like structure with the enamel. Although an element of chemical bonding also may exist with certain bonding resins that contain acid (e.g. Phenyl-P, PMDM), anhydride (e.g. 4-META), chelating (e.g. NPG-GMA), or other types of surface-active groups, the primary mode of adhesion to enamel is considered to be by micromechanical retention. However, superior tag formation and perhaps some chemical interaction may develop when certain types of surface-active components are used in the resin bonding system.

Because of its vital and heterogeneous nature, bonding to dentin has been a more challenging problem. On a weight basis dentin consists of 69% apatitic mineral (mainly hydroxyapatite), 18% organic matter (mainly collagen) and 13% water. Factors that can adversely affect bonding to dentin include an inherently wet, tubular surface structure that provides a variable area of peritubular and intertubular dentin. In addition, other complications that can adversely effect bonding include an ill-defined smear layer, which contains damaged dentin having denatured collagen and an altered mineral phase, and the potential for intertubular dentinal fluid flow to the bonded interface which may compromise the durability of the original bond to dentinal tissue.

Although many bonding systems for dentin are predicated on chemical reactions involving the mineral and/or organic components of dentin with surface-active agents (e.g. monomer, polymer, components of the initiator system, etc.), the prevailing assessment indicates that a strong micromechanical, interlocking mode of bonding is definitely involved. [28-38] In addition, in some systems, the polymerization mechanism, e.g. by initiation primarily from the dentinal substrate, may play an important role, especially in those systems (e.g. PMDM) that involve some sort of spontaneous polymerization and/or efficient oxygen scavenging reactions. A major objective of our studies has been to obtain a better understanding of all phases of the mechanisms for bonding to dentin which would aid in the design of more effective, durable bonding systems. Other objectives are to synthesize new types of surface active monomers, initiator systems or other agents for improving interaction with dentin and to assess the efficacy of new modes of pretreating dentin.

#### PROGRESS REPORT

##### Phase I Pretreatment of Dentin

Part (a) was deferred in favor of Parts (b) and (c) pending acquisition of necessary materials.

(b) Evaluation of pretreated dentin using functional monomers: mono(methacryloyloxy)ethyl maleate (MMEM)

Previous studies with mono(2-methacryloyloxy)ethyl phthalate (MMEP), a liquid aromatic homolog of PMDM, showed that this monofunctional surface-active monomer had promise as a dentin bonding agent. In this study the bonding efficacy of a liquid, monofunctional, aliphatic carboxylic acid monomer, mono(methacryloyloxy) ethyl maleate (MMEM) was compared to that of the similar aromatic surface-active monomer MMEP. (see Figure 1) Because of its relatively low viscosity it also was thought that MMEM may serve as a polymerizable surface-active solvent for the high melting, crystalline PMDM. Unfortunately, MMEM was not an especially good solvent for PMDM. The tensile bond strength (TBS) of bonding resins and an acetone solution containing MMEM were compared to the TBS of similar formulations containing MMEP. Dentin surfaces were pretreated sequentially with 6.8% w/w ferric oxalate in 2.5% w/w HNO<sub>3</sub>, 10% w/w N-phenylglycine (NPG) in acetone, and the experimental bonding resins before applying a chemically cured composite. The TBS of I-VI (n=10) shown in Table 1 were tested after 24 h storage in distilled water at 24°C. Significant differences exist between pairs (p <0.01) by the Student t test.

Fig. 1 STRUCTURE OF MMEP VS. MMEM VS. PMDM

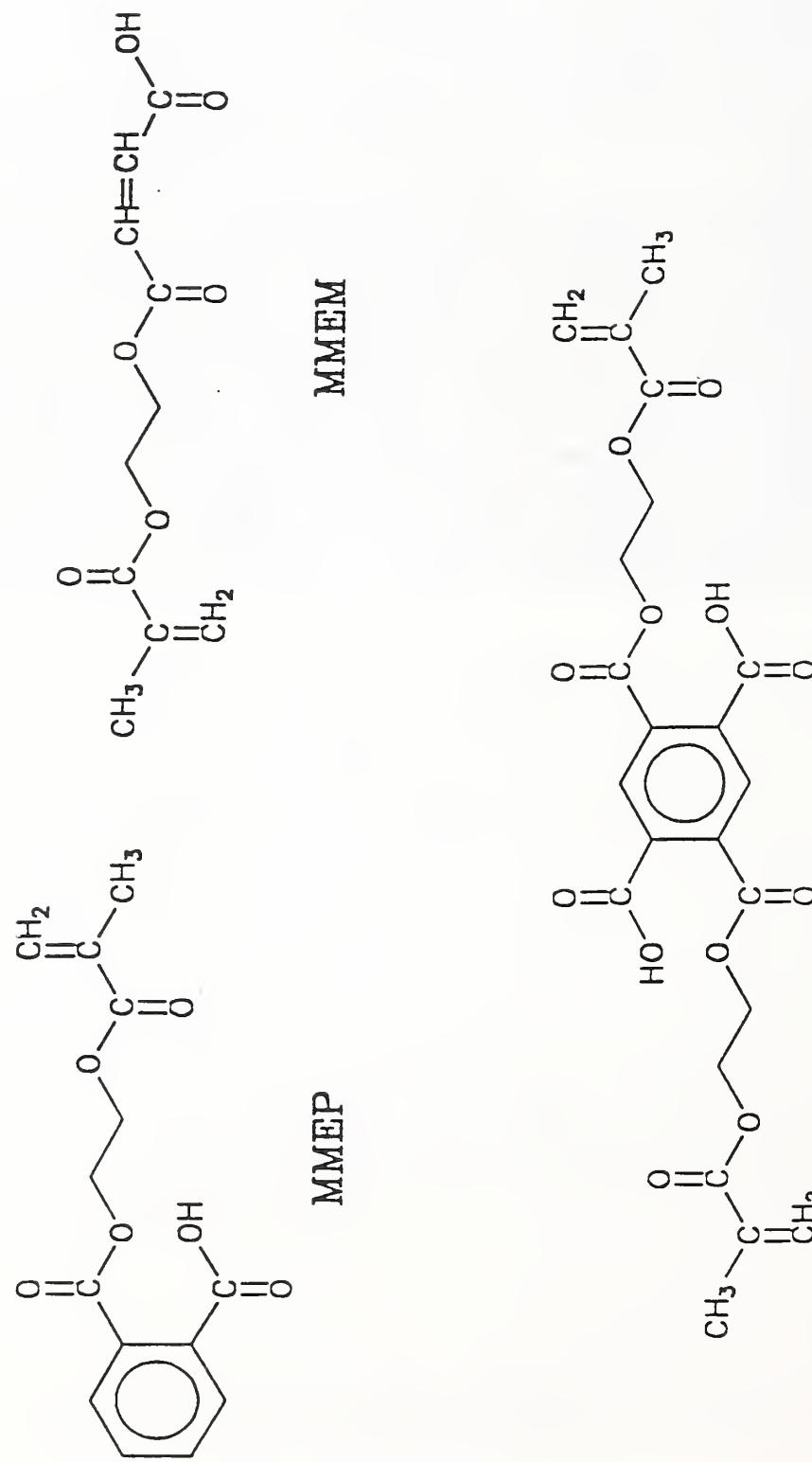


Table 1

## Comparative Tensile Bond Strengths of MMEM vs MMEP Bonding Systems to Dentin

<u>COMPOSITION OF BONDING RESIN IN % w/w</u>	<u>TBS (in MPa)</u>	<u>S.D.</u>
I. 20.7 MMEP in acetone (control)	8.7	2.2
II. 30.0 MMEM in acetone	1.0	2.3
III. 38.2 MMEP, 16.9 HEMA, 45.8 BIS-GMA	9.4	3.0
IV. 39.9 MMEM, 20.6 HEMA, 39.5 BIS-GMA	5.8	2.8
V. 7.2 PMDM, 59.4 HEMA, 33.4 MMEP	10.5	3.7
VI. 5.6 PMDM, 50.0 HEMA, 44.4 MMEM	0.6	1.9

The results indicate that surface-active bonding resins based on MMEM are not as effective in promoting a dentin/composite bond as formulations containing MMEP.

## (c) Pretreatment of dentin

1. Zirconyl chloride ( $ZrOCl_2$ )

An aqueous solution of zirconyl chloride ( $ZrOCl_2$ ) octahydrate was prepared (7.3 % w/w based on  $ZrOCl_2 \cdot 8H_2O$  or 3.2% w/w based on  $ZrOCl_2$ ). The pH, 0.85, was comparable to that of acidified ( $HNO_3$ ) aqueous ferric oxalate solutions usually employed in the three step bonding protocol for bonding composites to dentin using sequential applications of solutions of ferric oxalate, a surface-active amine (e.g. NPG) and PMDM. [37,38] In this preliminary study two sets of approximately ten dentin specimens were prepared as previously described and treated either with the aqueous  $ZrOCl_2$  solution or 6.8% purified ferric oxalate (FO) in 2.5% w/w aqueous nitric acid (control). Both sets of dentin were then treated with 10% NPG in acetone followed by an experimental bonding solution consisting of (59.4% HEMA, 33.4% MMEP, mono(2-methacryloyloxy) ethyl phthalate, and 7.2% PMDM (all percentages are on weight /weight basis). A chemically activated composite (ADAPTIC) was used in these studies. The 24 hour tensile bond strengths (n=10) obtained were 3.4 MPa (2.6 S.D.) for the  $ZrOCl_2$  pretreatment vs. 10.5 MPa (3.7 S.D.) for the FO pretreatment (control). Although the bonding achieved with this solution of  $ZrOCl_2$  was significantly less than that obtained with FO, microscopic and SEM examination indicated removal of the smear layer and alteration of the dentin surface by the treatment with  $ZrOCl_2$ . Other concentrations of  $ZrOCl_2$  solutions as well as solutions of other types of zirconium salts (e.g.  $ZrF_4$ ) are under investigation.

(2) L-ascorbic acid

L-ascorbic acid (vitamin C), a unique acid with antioxidant/activator properties, was evaluated as an etchant/conditioner for dentin. A 17.6% w/w solution of ascorbic acid (AA) in distilled water (pH=2) was applied to freshly cut human dentin sections for time intervals of 15, 30, 45, 60 and 120 seconds. The dentin sections were then rinsed with distilled water and air dried. The efficiency of removal of the smear layer from the treated dentin was evaluated using SEM. The optimal time for smear layer removal was 60 seconds. Tensile bond strengths (TBS) of a chemically cured composite (ADAPTIC) to dentin surfaces that were etched and conditioned with various AA aqueous solutions and sequentially treated with acetone solutions of NPG and MMEP were determined after 24 hour storage in distilled water at 24°C and compared to controls using FO/HNO<sub>3</sub> as the etchant/conditioner. The results are summarized in the following Table 2 (n = 10)

Table 2

<u>Concentration</u>					
	<u>AA (% W/W)</u>	<u>NPG (% W/W)</u>	<u>MMEP (% W/W)</u>	<u>TBS in MPa</u>	<u>SD</u>
A	32.0	10	17.3	8.9	1.9
B	25.0	10	20.7	7.7	2.5
C	17.1	10	20.7	7.6	2.5
D	30.0	5	23.2	6.2	1.9
E	25.0	5	20.7	6.8	3.3
CONTROLS					
F FO/HNO <sub>3</sub>	10		20.7	8.7	2.2
	5		20.7	8.1	2.4

From this study it was concluded that solutions of AA were effective both in smear layer removal and in conditioning dentin for bonding to composite using surface-active amines and surface-active monomers and, therefore, may be substituted for the acidified ferric oxalate (FO) in this bonding protocol.

## Phase VIII

### Investigation of the Self-curing Mechanism of PMDM and amines.

Since understanding the chemical aspects of the mechanism of bonding to dentin via the PMDM and related systems can aid in the design of improved dentin adhesive systems, we have decided to make this study part of our Phase I effort. Dr Farahani of the ADAHF/PRC is collaborating in this endeavor, especially with respect to radical detection and characterization using electron spin resonance (ESR) spectroscopy.

Spontaneous polymerization of PMDM has been observed on dentin preconditioned with acidic agents and surface-active amines. [28,37,38] The origin of this surface-initiated, autopolymerization remains unknown. A plausible mechanism for this may involve interaction of the acid groups ( $\text{CO}_2\text{H}$ ) of PMDM with the amine to form an ammonium salt which converts to initiating radicals via a charge-transfer complex. To test this hypothesis separate resin formulations containing component(s) with  $\text{CO}_2\text{H}$  groups (A), e.g. prepared using carboxylic acid monomers, organic acids, etc. were mixed with resin formulations containing various types of amines (B). Concentrations of the  $\text{CO}_2\text{H}$  and the amine components of A and B were varied and polymerizations were conducted at 23°C, 37°C and 60°C. Rotational hardening times (RHTs) were determined by mixing equal parts of A and B between crossed glass slides and noting the time to immobilization. RHTs varied inversely with temperature and directly with the concentrations of amine and acid. More acidic carboxylic acids (i.e. acids with lower pKas) favored polymerization while  $\text{O}_2$  inhibited the polymerization. Aromatic amines that are effective activators for the decomposition of benzoyl peroxide also are effective in activating the polymerization of  $\text{CO}_2\text{H}$ -containing resins. For example, N,N-dimethyl-p-toluidine was more effective than ethyl 4-dimethylaminobenzoate in promoting polymerization whereas aliphatic amines, even tertiary aliphatic amines, were much less effective.

$^1\text{H}$  NMR spectroscopy indicated ammonium salt formation and, in the case of the aromatic amines, changes which may be due to charge-transfer reactions. ESR indicates the formation of biradical species. The results suggest a radical polymerization mechanism involving acid-amine complexation and electron transfer such as that depicted in Figure 2.

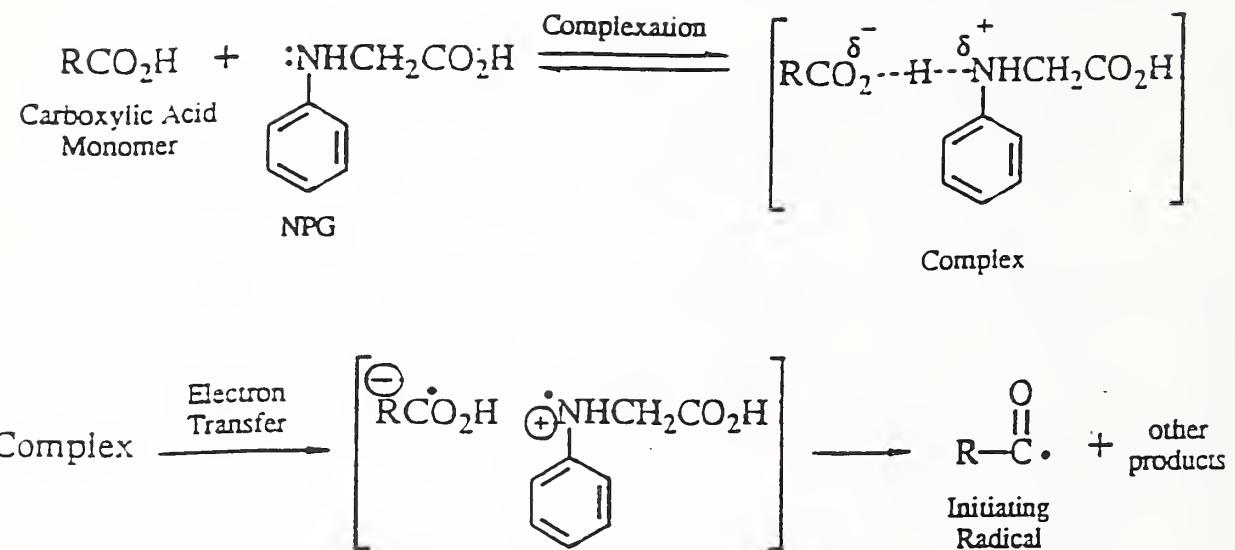


Fig. 2 MECHANISM FOR "SPONTANEOUS POLYMERIZATION" OF CARBOXYLIC ACID MONOMERS USING AMINE ACCELERATORS.

## E. Improvement of Dental Cements

### Background

Dental cements also can be considered as composite materials and because of their heterogenous nature exhibit many of the same problems, i.e. relatively weak matrices, fillers and interfaces that are vulnerable to mechanical, physical or chemical modes of degradation. [71-83] Dental cements are especially weak in their resistance to acidic conditions and the tensile and shear forces that are commonly generated by masticatory activities and stresses.

Dental cements can be divided into two broad categories: (1) those that are largely aqueous based (e.g. zinc phosphate, zinc polycarboxylate and glass ionomer cements) and (2) those that are relatively nonaqueous in nature, although small amounts of water or other protic agents are considered essential to their setting and hardening process (e.g. ZOE, ZOE-EBA, hexyl vanillate-EBA, and dimer acid cements). Dental cements that combine optimal strength, adhesion, durability and biocompatibility are still lacking.

The overall goal is to develop tough, durable cements by reducing their propensity to brittle failure and hydrolytic degradation, especially in acidic environments. By appropriate modification of the structure achieved by compositional changes in existing cements and/or by the development of improved types of composite structures, cements having these properties as well as enhanced biocompatibility and adhesiveness are expected.

### PROGRESS REPORT

#### Phase I

Develop new types of hybrid cement-composites based on polyelectrolyte cements and water soluble monomers capable of cyclopolymerization. The synthesis of the requisite monomers is progressing (see I A.4 part i) but is not at a stage to be applied to this study.

#### Phase II

Develop new types of hybrid cement-composites based on modified water soluble polymers.

The specific objective of this study was to determine how the addition of a flexible copolymer of maleic acid (shown in Figure 1) would affect the setting and working times and the diametral tensile strength (DTS) of two water-hardening glass ionomer cements.

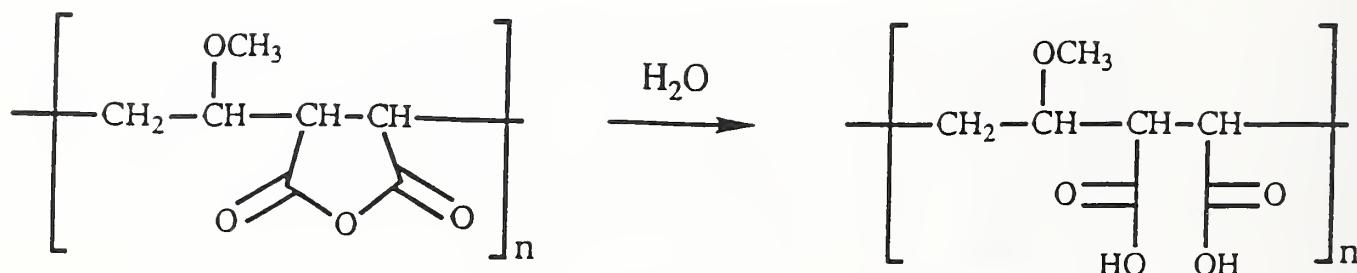


Figure 1 Molecular structure of PMVE-Ma (synthesized by hydrolysis of the corresponding maleic anhydride copolymer).

Poly(methyl vinyl ether-maleic anhydride, PMVE-MA (average molecular weight = 50,000; Gantrez AN-149, GAF Corp., Wayne, NJ) was converted to poly(methyl vinyl ether-maleic acid), PMVE-Ma, by hydrolysis. Various aqueous solutions of PMVE-Ma were prepared by heating aqueous mixtures of PMVE-MA at 60°C for 48 hours. Two of the solutions of PMVE-Ma, 3.5 and 4.5% w/w, were used in place of the liquid components of two commercial water-hardening glass ionomer cements, KETAC CEM and CHEMFIL II. The diametral tensile strengths (DTS) of each of these new types hybrid cements was determined after 24 hour storage in distilled water at 37°C (Table 1).

Table 1

<u>PMVE-Ma CONCENTRATION (w/w%)</u>	<u>POWDER P/L</u>	<u>DTS (S.D.)</u>
3.5	KETAC CEM, 4	9.2(1.4)
5.4	KETAC CEM, 4	8.7(2.6)
3.5	CHEMFIL II, 6	13.2(2.3)
5.4	CHEMFIL II, 6	13.0(3.2)
n=5		

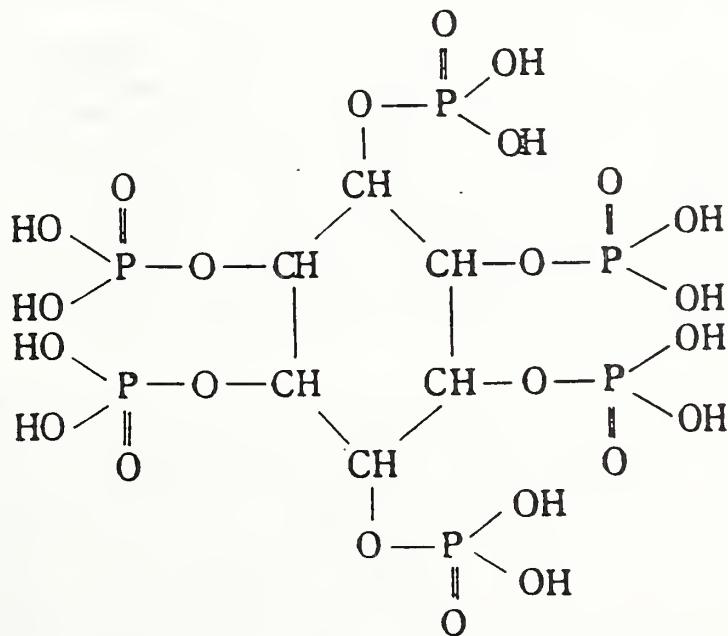
The DTS values as well as the working and setting times of these cements were similar to unmodified KETAC CEM and CHEMFIL II.

### Phase III

Develop new calcium phosphate cements based on the hydroxyapatite-forming reaction of anhydrous dicalcium phosphate (DCPA) and tetracalcium phosphate (TTCP) using aqueous solutions of phytic acid, derivatives or analogs as the reaction media.

A recently developed water-setting calcium phosphate cement (CPC) has the ability of setting under ambient conditions and, because of the similarity of its composition to that of the mineral component of bone and tooth, of yielding a highly biocompatible cementitious material. [80] Because of these properties, this cement potentially has a wide range of applications in medical and dental practice. However, the relatively slow hardening process and comparatively modest mechanical strength and brittle nature of CPC currently limit it to non-stress bearing applications. Recently in an attempt to overcome these disadvantages, the reaction between the tetracalcium phosphate (TTCP) and anhydrous dicalcium phosphate (DCPA), the two major components of this cement powder, has been studied in the presence various water soluble polymers. [81,82] For example, aqueous solutions of poly(alkenoic acids), especially poly(acrylic acid), produced cements that were much faster setting and had higher compressive strength than CPC. [82] The formation of hydroxyapatite was, however, markedly reduced. In addition, the cement-forming reaction of poly(acrylic acid) and similar polyacids with CPC powders was too fast to permit easy handling of the cement and required additives to control the rate of setting. [82]

In this study, the reactions of aqueous solutions of phytic acid and those of a less reactive polyacid, the hydrolyzed version of a 1:1 copolymer of methyl vinyl ether and maleic anhydride (PMVE-MA), with CPC powders were investigated.



Phytic acid, myo-inositol hexaphosphate (Figure 2), is a naturally occurring polyfunctional acid that has been shown to have cement-forming properties with zinc oxide and

various aluminosilicate glasses. [83] The matrices of these cements are thought to be halatopolymeric in nature. The anhydride copolymer, which is offered in several grades (Gantrez AN-119, 139, 149 and 169, GAF Corporation), can be dissolved in water with hydrolysis of the anhydride groups to form the corresponding maleic acid copolymer, PMVE-Ma. The primary carboxyl group of the hydrolyzed copolymer has a  $pK_{a_1} = 4.65$  while the secondary carboxyl group has a  $pK_{a_2} = 8.70$ . [100] This copolymer already has a number of nondental applications, e.g., hair sprays, surgical adhesives, etc. which suggest potential favorable biocompatibility for dental and other biomedical uses. [101] The object of this study was to assess the feasibility of forming polymeric calcium phosphate cements (PCPC) from CPC powders or similar calcium compounds and aqueous solutions of either phytic acid or of PMVE-Ma.

In this part of the study the cement forming properties of phytic acid with calcium phosphate cement (CPC), powder (a stoichiometric mixture of DCPA and TTCP) were investigated. Aqueous solutions of phytic acid of various concentrations (w/w percent) were prepared, i.e. 0.1, 0.4, 0.8, 5.0, 10.0, 15.0, 20.0, 40.0, 50.0 and 73%. With the lower concentrations of phytic acid (0.1-5.0%) either non-setting or very slow setting cements resulted even when high powder/liquid (P/L) ratios were used. The cements were very weak and decomposed in water. The more concentrated phytic acid solutions tended to give unworkable pastes with CPC powder, even at low powder/liquid ratios, due to the extremely fast-setting behavior of these mixtures.

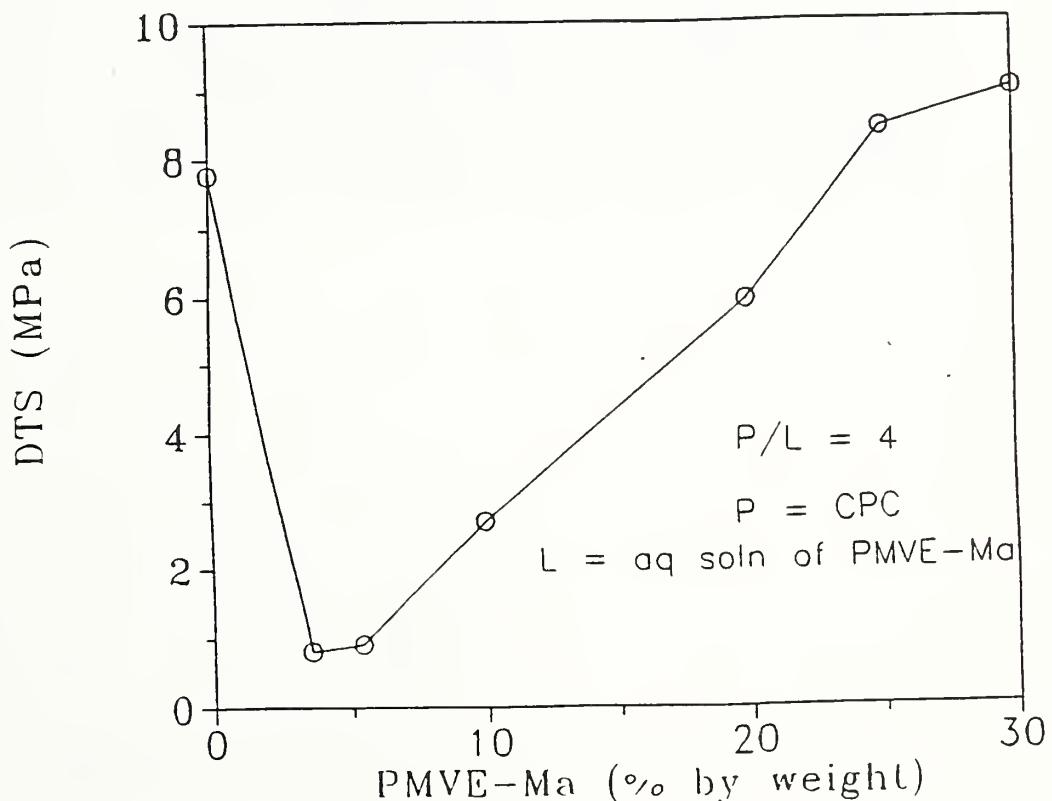
The 73% phytic acid solution did form potentially useful cements with zinc oxide (ZnO), aluminosilicate and calcium metasilicate powders. With the powder component of Tenacin (mainly ZnO), P/L=2, a fast-setting cement was formed having a diametral tensile strength of 6.0 MPa (0.5 S.D.) n=5. Similarly, this solution with the calcium aluminofluorosilicate glass powder (P/L=1.5) of Fuji III glass ionomer cement had a DTS of 7.6 MPa (0.8 S.D.). With the basic calcium metasilicate powder (P/L=2), a cement with a DTS of 6.2 MPa (1.2 S.D.) was obtained.

The second part of this study to develop improved types of polymeric calcium phosphate cements (PCPCs) was concerned with the feasibility of obtaining useful cementitious products from the reaction of poly(methyl vinyl ether-maleic acid), PMVE-Ma, with CPC powder or its components. The rationale for using PMVE-Ma in contrast to other polycarboxylic acid polymers is that this polyacid has greater flexibility and a lower carboxylic acid content. Both of these properties would be expected to moderate the

brittle nature of these polyelectrolyte cements by providing more flexible, less highly crosslinked matrices for the PCPCs. The lower carboxylic acid content also was expected to moderate the usual fast-setting behavior of PCPCs based on polycarboxylic acid polymers.

Various aqueous solutions of a PMVE-Ma with an average molecular weight of 50,000 were prepared, i.e. 3.5, 5.4, 10.0, 20.0, 25.0 and 30.0% w/w. Figure 3 summarizes the effect of PMVE-Ma concentration on the DTS of the PCPC that results from mixing these solutions with CPC powder at a P/L=4. More concentrated solutions of PMVE-Ma (e.g. 35% w/w) were too viscous and could not be mixed with CPC powder at this powder/liquid ratio. In contrast to the extremely fast cement-forming reactions of poly(acrylic acid) and similar polyacids with CPC powders, the setting times for the PMVE-Ma cements were significantly longer (e.g. 30 min. for 30.0 w/w PMVE-Ma).

Effect of PMVE-Ma Concentration  
on DTS of PCPC Cements



Infrared analysis of the set cement showed that the carbonyl stretching band ( $1635\text{ cm}^{-1}$ ) of the carboxylic acid groups of PMVE-Ma had disappeared and two bands attributable to carboxylate ( $-\text{CO}_2$ ) formation were observed at  $1558\text{ cm}^{-1}$  and  $1418\text{ cm}^{-1}$ , indicative of neutralization reactions involving PMVE-Ma and CPC powder.

By x-ray diffraction analysis no hydroxyapatite was detected in the set cement, but the ratio of intensity of x-ray peaks for TTCP/DCPA decreased, indicating that TTCP was consumed in the hardening reaction. As the more basic component of the CPC powder this is not surprising and is consistent with previous results regarding the reaction of polycarboxylic polymers with CPC powder. [81,82]

In Table 2, the mechanical properties of the PCPC for the 30% w/w PMVE-Ma aqueous solution were compared with those of CPC (control, derived from CPC powder plus 25 mmol/L aqueous  $\text{H}_3\text{PO}_4$  containing 1.32 mmol/L of sodium fluoride) and a commercial glass ionomer cement (KETAC CEM; ESPE-PREMIER). The diametral tensile (DTS), compressive (CS) and flexural strength (FS) of this PCPC were greater than that of the control (CPC). Compared with the glass ionomer cement (GIC), the PCPC was only lower in its compressive strength, which is similar to that of zinc polycarboxylate cements. However, by its fracture behavior, the PCPC appears to be a tougher, less brittle cement than either GIC or CPC. Determination of an accurate setting time for this PCPC by the Gillmore needle test proved difficult as the cement exhibits a prolonged elastomeric stage before it hardens sufficiently to resist indentation. An approximate setting time of 30 minutes was determined from three specimens.

Table 2

Comparison of Physical Properties of a Polymeric\*  
Calcium Phosphate Cement (PCPC), a Calcium Phosphate  
Cement (CPC) and a Glass Ionomer Cement (GIC)

Cements	P/L	DTS (S.D.)** in MPa	CS (S.D.)** in MPa	FS (S.D.)** in MPa
PCPC	3.0	13.57 (1.24)	65.76 (4.37)	25.46 (3.64)
CPC	4.0	7.77 (1.26)	46.10 (10.21)	19.94 (1.62)
GIC***	4.0	8.87 (2.30)	122.40 (23.37)	12.81 (4.73)

n=6

\* PMVE-Ma, 30% w/w aqueous solution

\*\* After 24 hours storage in distilled water at 37°C

\*\*\* Ketac Cem (ESPE, Germany)

F. **Fluorescent Probes for Assessing the Cure of Dental Composites and the Effectiveness and Durability of Coupling Agents**

**PROGRESS REPORT**

**Objective**

The primary objectives of this proposal are to explore the use of fluorescent dye technology for improvement of the properties of dental composite resins and resin-based cements through: 1) monitoring of the degree of cure and 2) assessing the quality of the filler-matrix interfacial bond within composites.

The first application involves the use of cure sensitive fluorescent dyes for making definitive measurements of the degree of cure in resins, composites, and cements, thereby leading to improved resin formulations and initiator systems. It can be foreseen that this technology could be useful for both research and product quality assurance.

The second application is the use of fluorescent dyes for the quantifying the effectiveness of various methods of applying coupling agents to filler substrates and for determining the degradation resistance of the coupling agent-to-filler interfacial bond. This work also holds the potential for the evaluation of the durability of the interfacial bond between the resin matrix and the coupling agent-filler system.

**Background**

Fluorescent probes, in the form of relatively low molecular weight organic dyes (usually with substituted aromatic structures), absorb light energy (UV and/or visible) at characteristic wavelengths and emit a spectrum of light at longer wavelengths. Some fluorescent molecules exhibit sensitivity to viscosity and to the chemical environment, such as polarity, solvation, and pH, at the molecular site. [102-106] Thus since the microviscosity of a resin based system changes with degree of cure, fluorescent probes hold the potential as a real time indicator of how well the system has cured. Fluorescent probes also might be useful as tracer molecules to indicate the extent of the silanization of filler particles.

These fluorescent probes can be uniformly dispersed in the resin or attached to various functional molecules (through double bonds or amino groups). The spectral characteristics of the fluorescent probe can change in several ways (depending on the microenvironment in which the probe

resides) including: wavelength (color) shifts in peaks of the emission spectra, changes in the fluorescent intensities (i.e. changes in peak heights), and/or changes in the shape of the emission spectra.

The selection of suitable fluorescent probe molecules for degree of cure studies is governed by the following considerations: (1) chemical stability in the cure environment (e.g. how are results affected by chemical reactions involving the probe, e.g. reactions with the photo-oxidant), (2) sensitivity of the fluorescence intensity to a wide range of microviscosities, (3) excitation and fluorescence frequencies in relation to the internal photochemical effects of the resin systems, (4) solubility in the resin, and (5) the excitation and fluorescence frequencies of any internal, non-viscosity dependent, fluorescent intensity standard. The selection of probes for efficacy of silanization requires that the probe be easily chemically attached to the silane molecule and that the new bond be chemically stable. To assess the quality of the silanated interface requires that the fluorescent probe exhibit sensitivity to the viscosity of the microenvironment created by solvation of the surface modified filler (similar to the probes used in the degree of cure studies).

One difficulty encountered with the use of fluorescent dyes for the assessment of degree of cure or effectiveness of silanization in glass filled composites is the phenomena of light scattering. The presence of the fine particulates adds scattering peaks to the fluorescence spectra of composite samples. These scattering peaks can be subtracted out from a reference spectrum, but more work remains to be done to assess the reproducibility of such spectrum subtraction techniques. An additional note should be made here that the original intent to use fiber waveguides for fluorescence monitoring has not been pursued as yet because the basic analytical technique requires further development before this application can be considered.

#### OBJECTIVE 1: CURING TECHNOLOGY

This section presents the results of progress from the one year (20% man year effort) pilot study on fluorescent cure technology and serves as the basis for a request for an extension of the work through FY's 92 and 93.

##### Overview

Fluorescent probes that were identified for sensitivity to changes in the microviscosity fell into two classes: 1) the

excimer type, and 2) combination of a viscosity sensitive dye and an insensitive dye, the latter of which serves as an internal intensity standard. Probes of the excimer type exhibit dual fluorescence with emissions arising from monomeric units and from an excimer formation which results when two chromophors are situated such that the electronic excitation of one chromophor is shared with the other through dipole coupling. [107] Emission from the excimer state occurs at a lower frequency than that from the excited monomer. Excimer type probes exhibit a decrease in excimer fluorescence due to the decreasing diffusion coefficient with cure. [108]

The other class of fluorescent probes to monitor cure are those that show sensitivity of the fluorescence spectra to the local viscosity, or as it is sometimes called, microviscosity, due to the dependence of the internal modes of rotation of molecular bonds on microviscosity [106,109-113]; these are the type of fluorescent probes utilized in this report. An electronically excited molecule returns to the ground state either by giving off radiation (fluorescence) or by transferring the electronic excitation into vibrational or rotational degrees of freedom (non-radiative). Non-radiative transition probabilities depend on molecular mobility, in particular internal rotations. Thus fluorescent probes that are sensitive to local environmental conditions exhibit fluorescent spectral changes that arise because of the competition between radiative and non-radiative processes for de-excitation of the electronically excited states, a change which occurs as the cure proceeds. [107] A probe molecule constrained by its environment so as to limit internal rotations, as would occur during gelation and continues through the polymerization process, would exhibit increased fluorescence since non-radiative pathways become more restricted.

### Accomplishments

Phase I Develop dye systems which are physically and chemically compatible with dental monomers.

Fluorescent measurements were made on the SPEX FLUOROLOG (series 2) with set detector voltages (900 volts and 550 volts) and monochrometer slit widths of 1.25 mm. No instrumentation corrections were made for wavelength inaccuracies within our device. The resin samples were originally contained in screw cap pyrex vials, and the fluorescence measurements were made on the front surface of the samples. The resin systems used were mixtures of different ratios of BIS-GMA and TEGDMA. Camphorquinone (CQ), shown in Figure 1a (0.2% by weight), was used as the photosensitizer activated by the blue light source (MAX

LITE, Caulk/Dentsply). Ethyl p-dimethylaminobenzoate (4EDMAB), shown in figure 1b, was used as the tertiary amine photo-activator (0.8% by weight). The first fluorescent dye tested in this phase was 6-propionyl-2-dimethylaminonaphthalene (PRODAN), the structure of which is shown in Figure (1c). PRODAN is a viscosity and polarity sensitive probe that exhibits a shift in wavelength toward the blue end of the spectrum as the viscosity of the resin mixture increases and as the polarity of the solvent or resin decreases. Resin formulations made with the addition of  $10^{-5}$  M PRODAN in 100% TEGDMA exhibited a broad fluorescence maximum in the uncured state between 430 nm and 450 nm when excited at 360 nm which is the excitation spectrum maximum. When the more viscous BIS-GMA was tested with PRODAN the emission maximum was at 415 nm. Upon curing of the resins the emission maximum for all mixtures was found to be at 415 nm and this value was reached immediately after exposure to the blue light. This indicated that the range of viscosities that could effectively be investigated with this probe using these monomers was very limited.

Other problems were also encountered with the use of PRODAN as a cure monitoring fluorescent probe in dental resin systems. Firstly it was determined that PRODAN itself was acting as an activator for the camphorquinone in the curing stage as could be seen by the initial drop of the fluorescent intensity followed by a gradual increase. Evidently PRODAN was complexing with camphorquinone through exiplex formation. Furthermore the presence of camphorquinone itself changes the emission spectrum of fluorophors that have emission spectra between 450 and 490 nm. Finally, it was discovered that the tertiary amine photoactivator used in these studies (4EDMAB), a photoreductant for the photooxidant (CQ), was itself highly fluorescent in the cured resin but not so in the uncured state.

The second part of this phase of the research concentrated on the fluorescent behavior of 4EDMAB in a 1 to 1 (wt/wt) mixture of BIS-GMA and TEGDMA. The purpose was to use this model system for investigating the potential for direct correlation of the probe fluorescence with the degree of cure obtained using infrared (IR) spectroscopy. In this case the curing activator and the fluorescent probe are the same molecule. Two problems were encountered in the curing of the resin in a pyrex vial : 1) the sharp spectral cutoff from pyrex at 350 nm made excitation scans of 4EDMAB impossible and 2) the sample geometry was so large (3 mL) that a substantial exotherm was produced upon curing which made isothermal cure measurements impossible. To overcome these problems, we switched to using flat, thin quartz cells

for sampling the resin. These cells were assembled from a flat quartz plate and a quartz plate with a recessed trough. The dimensions of the samples formed in the flat quartz cell are 1.5 mm thick with a surface area of 8 mm by 30 mm. The cavity of the flat cells was positioned at the focal point of the excitation beam. Because the quartz plates transmitted more light than the pyrex containers, the fluorescent intensity increased dramatically with the use of the thin quartz cells, and thus smaller monochrometer exit slits (0.25 mm vs 1.25 mm) were utilized.

The fluorescent effects of 4EDMAB have been investigated previously. [109,112] These types of molecules exhibit dual fluorescence corresponding to two kinds of excited states, denoted A\* and B\* states. According to the theory first proposed by Grambowski et al [114], 4EDMAB molecules are characterized by twisted intramolecular charge transfer (TICT) between the amino group and the aromatic ring. In the excited state the donor part (dimethylamino group) of the initially planar molecule rotates round the amino-phenyl bond. This is accompanied by the development of a charge separation between the donor and acceptor moieties [112]. In polar solvents the twisted polar A\* state can be stabilized by solvent reorientations, so that the A\* band appears at longer wavelengths relative to the planar, non-CT B\* band. Thus the fluorescence of these types of molecules show sensitivity to the solvent polarity as well as the medium viscosity.

In the work presented here the most dramatic change of the fluorescence emission of 4EDMAB was the change in the intensity of the B\* band. In the uncured resin the A\* band was positioned at 460 nm and the B\* band at 360 nm when excited at 330 nm (Figure 2). The A\* band appeared to change position slightly with cure, but the intensity of the B\* band increased over 20 fold (Figure 3). This increase in intensity of the B\* band is presumably due to the fact that the molecular rotation is restricted in the cured resin and more of the absorbed UV energy is transferred to radiative fluorescence at the B\* band than through non-radiative losses and solvent quenching.

The change of the excitation spectrum of 4EDMAB in the resin system is shown in Figure 4 along with the excitation spectrum of (2EDMAB) (note that the fluorescence in the cured 4EDMAB samples is about 20 times as strong as in the uncured state).

To investigate the effects of the molecular structure of the probe on the fluorescence of this TICT (Twisted Internal Charge Transfer) type probes, a brief study of the fluorescence of the three EDMAB isomers was conducted. The

excitation spectra and the emission fluorescence of the meta and ortho isomers (3, 2 isomers) of ethyl dimethylaminobenzoate in the uncured resin (BIS-GMA/TEGDMA 1:1) and in the cured state are shown in Figures 6-9). The excitation spectra and fluorescence of (dimethyl-p-toluidiene), Figure 1d, (a much less polar amine analog of 4EDMAB) is also shown in Figures (10 and 11). These results indicate that the para-substituted 4EDMAB, which has a fluorescence emission peak at 365 nm in the cured resin and substantial fluorescence quenching due to non-radiative energy pathways in the uncured state, behaves considerably different than the other isomers. The ortho substituted molecule is highly fluorescent in the uncured resin and has an emission maximum at 415 nm. Upon curing with the 2EDMAB only a 10% increase in the fluorescent intensity was observed with no shift in the peak wavelength. This is consistent with the concept of restriction of internal rotation leading to an increase in fluorescence intensity. In this case however the ortho-substituted 2EDMAB molecule already has restricted motion in the uncured resin due to steric hinderance existing between the amino functionality and the benzoate group. The meta substituted 3EDMAB molecule does not have the amino and benzoate groups in conjugation through the aromatic ring. In this case, the initial uncured spectrum was quite strong with two maxima at 420 nm and 450 nm. Upon curing of this resin system a 2.5 to 3 fold increase in the emission intensity was observed along with a minimal shift in the peak position to around 415 nm, which is at a much longer wavelength than for the para-substituted isomer. The final emission intensity was the highest observed. Neither of the other substituted (3, and 2) EDMAB probes exhibited sensitivity to the microviscosity. The fluorescence of dimethyl-p-toluidiene (Figure 1d), a dimethylamino benzene without the carboxylate functionality, was very weak in the uncured resin as was the 4EDMAB and only increased two fold after curing.

Finally composites were formulated with 4EDMAB in a BIS-GMA/TEGDMA resin mixture. The cured composite showed the same intensity increase at 365 nm in the fluorescence emission spectrum as the resins alone. However, the emission spectrum was also changed by the addition of scattered light from the glass particulate filler.

#### Phase II Correlate fluorescent dye measurements with those from IR spectroscopy for quantitative assessment of degree of cure via fluorescence.

In this phase of the project infrared spectroscopic techniques were used to correlate the IR degree of cure with changes in the fluorescence intensity of the 4EDMAB B\* peak at 365 nm (excitation at 345 nm) as cure proceeded with

time. Although the position of the 4EDMAB B\* peak is a weak function of excitation wavelength (shorter excitation wavelength gave blue shifted emission peaks), for a given excitation wavelength this peak did not shift position as the cure proceeded. The resin used was a 1:1 mixture of BISGMA and TEGDMA (CQ = 0.2%, 4EDMAB = 0.8%). All fluorescent measurements were done in thin quartz cells with an excitation wavelength of 345 nm. Relative intensity measurements were accomplished by dividing the final intensity by the starting fluorescence intensity at 365nm. The cure conditions are listed below:

- 1) Sample cured at room temperature for 60 seconds with the Caulk Max Light with fluorescence measurements of the same sample after 2, 5, 10, 30, and 60 minutes (representative spectra shown in Figure 3).
- 2) Sample cured at room temperature for 60 seconds and then immediately put in 60 °C oven for 1 hour. (Figure 5)
- 3) Sample cured at room temperature for 18 second with subsequent fluorescent measurements at 2, 10, 20 and 30 minutes.
- 4) Sample with reduced camphorquinone concentration (0.05%) cured at room temperature for 6 seconds with fluorescent measurements taken at 2, 10, 20 and 30 minutes.

The results of the fluorescent intensity changes with time for the different sample preparations are shown in Figure 12 (note logarithmic time scale).

The IR degree of cure was determined by measuring the relative peak height of the double bond at 1637  $\text{cm}^{-1}$  relative to the aromatic peak at 1582  $\text{cm}^{-1}$ . Baseline subtraction methods were employed since both of these peaks are shoulders of the strong aromatic peak at 1608  $\text{cm}^{-1}$ . This was accomplished by drawing a baseline from either end of the spectrum scan (1660  $\text{cm}^{-1}$  and 1550  $\text{cm}^{-1}$ ) to the shoulder region at 1590  $\text{cm}^{-1}$ . IR degree of cure measurements were made under several conditions as described below.

- 1) Sample between mylar sheets with a 4 $\mu\text{m}$  spacer were cured with a Caulk Max Light for 60 seconds; the mylar was removed at various time intervals (ie. 2 min, 10 min, and 60 min).
- 2) Sample is cured the same as 1) except it is then immediately put in a 60 °C oven for 60 minutes.
- 3) Sample between KBr windows was cured by a Caulk Max Light for 18 seconds.
- 4) Sample, with reduced camphorquinone concentration (0.05%), was cured for 6 seconds between KBr windows.

The results of the IR degree of cure vs time for the different curing conditions are shown in Figure 13. Combining data from Figures 12 and 13 gives the correlation between fluorescence intensity changes and IR degree of cure, as shown in Figure 14, and Table I. Curing conditions 1) and 2) were very reproducible since the curing is not light limited (60 seconds of light exposure); however, the range of degree of cure is relatively limited (56% to 64% for condition 1, and 75% for condition 2). Conditions 3) and 4) were more difficult to perform since the films were not coherent at short times and we relied on direct curing of the resin through the KBr windows, which resulted in gluing KBr windows together. The lack of linearity seen in Figure 14 may be due to the fact that the very thin film between the KBr blocks has less of an oxygen reservoir than the larger samples used in the fluorescent measurements and thus are cured more completely. A more accurate correlation should result by using equivalent sample sizes in the two types of experiments. However for demonstration purposes the results are entirely satisfactory. Some efforts were given to identify an internal standard probe to normalize the fluorescence intensity. One such probe tried was DTBP-PDC (Perylene derivative shown in Figure 1e). The fluorescence of this probe, however, was not constant after exposure to the blue curing light, indicating that some interaction with the resin formulation was occurring.

Table 1

Correlation of Fluorescence Intensity Ratio  
with IR Degree of Cure

Time (Min)	60 seconds cure 20°C		6 s. CQ = 0.05%		18 s. cure 20°C	
	I <sub>t</sub> /I <sub>0</sub>	DC	I <sub>t</sub> /I <sub>0</sub>	DC	I <sub>t</sub> /I <sub>0</sub>	DC
1	18.5 (.4)	54.2 (1.6)				
5	20.2		3.2	13.5	10.0	43
10	20.4 (.3)	60.5 (3.5)	4.4	23.6	11.9	45
20	20.6 (.3)		5.8	30.3	13.5	48.5
30	21		6.7	36.3	15.0	50
60	21.5 (.2)	63.8 (0.7)				
*60°C 1 h	25.3 (.2)	75 (1.8)				

#### OBJECTIVE 2: COUPLING-AGENTS

This section presents the results from the one year (10% man year), pilot study on the use of fluorescent dyes for the

evaluation of efficacy of coupling agents, and serves as the basis for a request for an extension of the work through FY's 92 and 93.

### Overview

Quantitative techniques for determining the effectiveness of applying coupling agents for bonding of the glass filler particles to the resin matrix and for monitoring the persistence of these interfacial bonds can be useful for developing composite restorative dental materials which are more durable. Comparatively few studies on the effectiveness of silanization have been reported. Most of these studies rely on complicated FTIR measurements, or indirect evaluation of strength properties of composite materials.

The use of fluorescent dyes offers two methods for determining the durability of silanization. The first method relies on the chemical attachment of a fluorescent probe to a small fraction of silane molecules attached to glass fillers or other model substrates. The fluorescent intensity of the probed silane on the glass can be used to monitor the effectiveness of attachment. Conversely, the fluorescence intensity after exposure to degradative environments can be measured to quantitatively monitor the amount of hydrolysed silane escaping from the fillers into the degradative solutions. At low concentrations a linear relation exists between the concentration of the probed silane and the fluorescent intensity.

The second method of assessing the durability of silanization involves the probing of silanized fillers which are then used to make model composite materials. If appropriate fluorescent probes are identified (ones which have a high sensitivity to local solvation and microviscosity) it is anticipated that quantitative information can be obtained on the stability of the coupling agent-filler bond with time by observing the color shift of the fluorescent emission spectra. Such color shifts may also provide information regarding the combined effects of mechanical and chemical debonding.

### Accomplishments

Phase I Evaluate the efficiency of silane attachment on flat plates by fluorescence measurements.

The initial intent of this phase of the research involved silanizing flat quartz plates with 3-aminopropyltriethoxy silane (APS). Then a fluorescent probe, fluorescein isothiocyanate (FS-NCS) (see Figure 1f), was reacted in dry acetone with the silanized quartz plate. Subsequently the

side of the plate with the probed silane was to be held in contact with various solvents (to solvate the fluorescent probe) and fluorescent intensity changes would quantitatively indicate the amount of probe and consequently the amount of silane left on the surface after soaking in various solvents. Difficulties were encountered, however, in achieving a uniform silane layer on the quartz slides. The low surface area of the flat plate meant that either too little fluorescent intensity was observed or that thick multilayers of silane would clump on the surface, most of which apparently oligomerized but did not necessarily become covalently attached to the quartz surface.

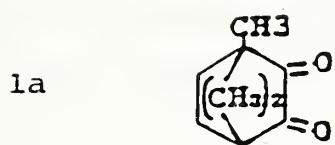
Subsequent experiments concentrated on the silanization of actual filler particles, Corning 7724 glass, with APS. The surface area of the particulate glass is several orders of magnitude larger than that of a flat plate and more uniform layers of covalently bonded silane could presumably be formed due to the larger number of chemically active sites on the glass particles. The silanized glass was then reacted with a different probe, DANSYL-NCS the structure of which is shown in Figure 1g, at a concentration that would probe about 1 in every 180 silane molecules. DANSYL-NCS was used in these experiments because it was easier to use and apparently did not physically absorb onto the glass as readily. Furthermore it is anticipated that the dimethylamino moiety on the DANSYL-NCS may exhibit viscosity related effects that could be useful for analyzing the silane interface in actual composite formulations. The fluorescent intensity of the DANSYL-NCS reacted, APS treated glass reaction mixture was then traced over time. It was found that the reaction proceeded very quickly with the amino silanized glass (40% complete after 60 seconds in contact with glass and more than 99% complete after 2 hours, with constant stirring of the mixture). An additional experiment was conducted in which the silane was reacted with the DANSYL-NCS probe in solution before being attached to glass filler particles. This reaction was also found to proceed to completion very quickly.

Phase II For the most promising systems from phase I, evaluate the stability of silane attachment after immersion in water and other solvents.

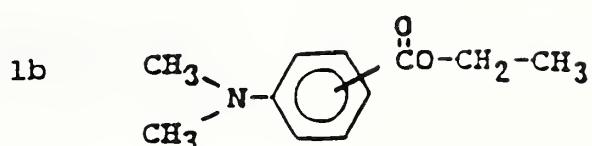
In this phase of the research the DANSYL-NCS probed APS-silanized glass particles (0.5 gram) were placed in various solvents (10 mL) for periods of 2 hours, 1 day, and 5 days. The solvents tested were dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), absolute ethanol, water, and a 1:1 ethanol-water mixture. The glass-solvent mixtures were then monitored for fluorescent intensity to assess the amount of silane that had been

hydrolyzed or decoupled from the glass surface. The suspensions of the solvents with the glass powder could not be decanted or adequately centrifuged (300 RPM for 10 minutes) to remove all of the suspended particles, which caused excessive light scattering in the fluorescence measurements. Separation of the glass particles from the solvents was accomplished by filtering the suspensions through fluorinated (non-reactive) 0.45  $\mu\text{m}$  membrane filters. Although the intensity measurements were somewhat erratic, with time several observations can be made. First, when the silanized and probed glass was placed in either dichloromethane, ethanol, or water, less than 2% of the silane went into solution. With the ethanol-water mixture however as much as 7.5% of the silane appeared to be hydrolyzed after 2 hours. One potential difficulty in the quantitative analysis of silanization is the problem of silane oligomerization in solution. This polymerization type reaction can tie up free silane and thus may bias the results.

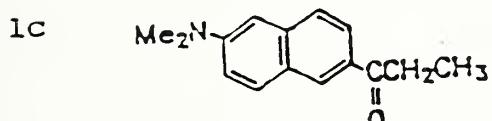
CHEMICAL STRUCTURES (FIGURE 1 a-h)



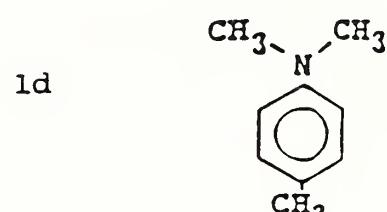
camphorquinone (CQ)



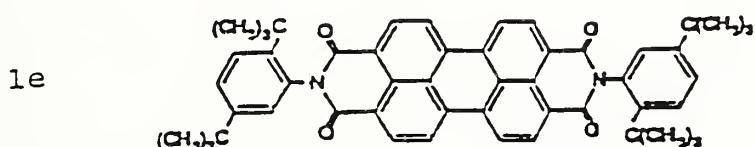
ethyl dimethylaminobenzoate  
(EDMAB)



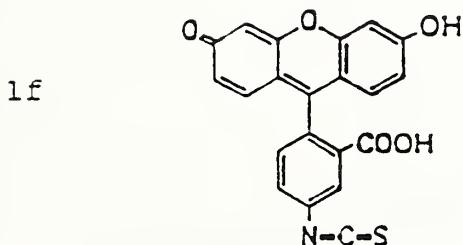
6-propionyl-2-dimethylaminonaphthalene  
(PRODAN)



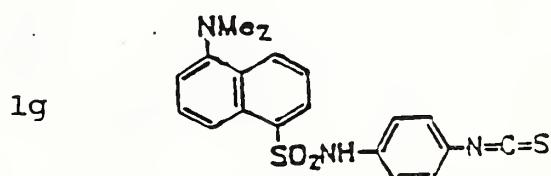
dimethyl-p-toluidine  
(DMPT)



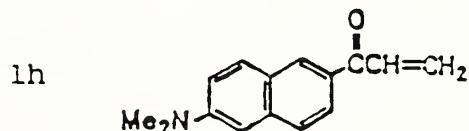
*N,N'-Bis(2,5-di-tert-butylphenyl)-3,4,9,10-perylene dicarboximide.*  
(DTBP-PDC) (Perylene derivative)



fluorescein-5-isothiocyanate  
(FLUORESCEIN-NCS)



p-(5-dimethylaminonaphthalene-1-sulfonyl)  
aminophenylisothiocyanate  
(DANSYL-NCS)



6-acryloyl-2-dimethylaminonaphthalene  
(ACRYLODAN)

Fig. 2

## Fluorescence of 4EDMAB Pre-Cure

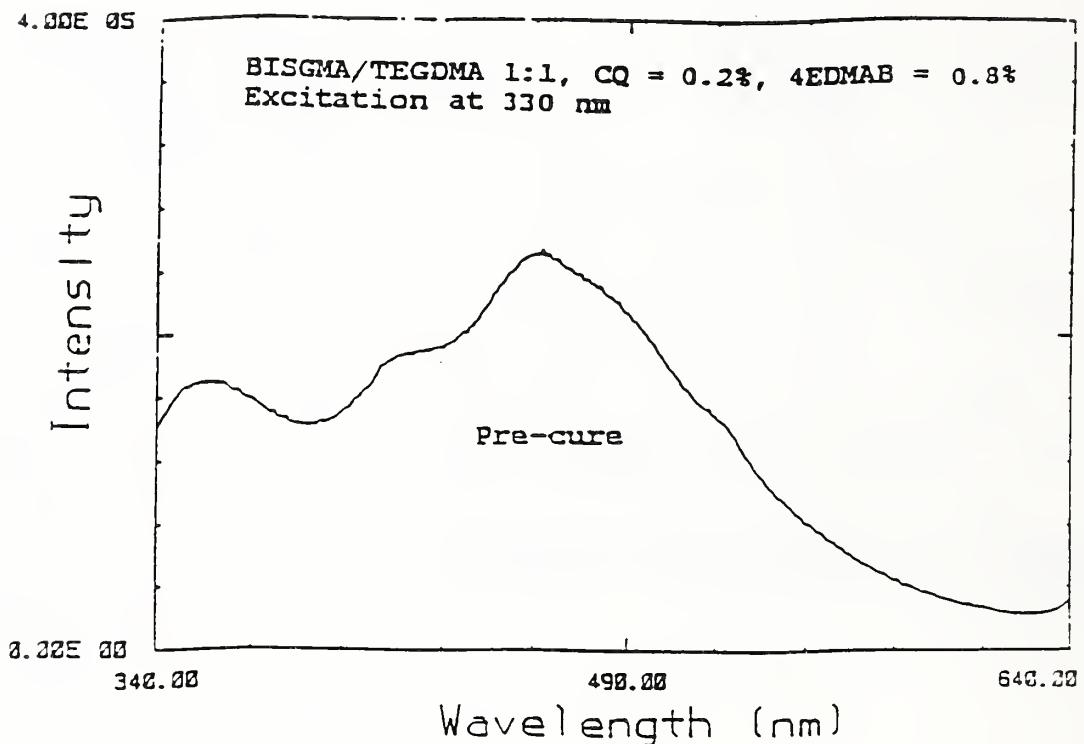


Fig. 3

## Fluorescence of 4EDMAB with Cure Time

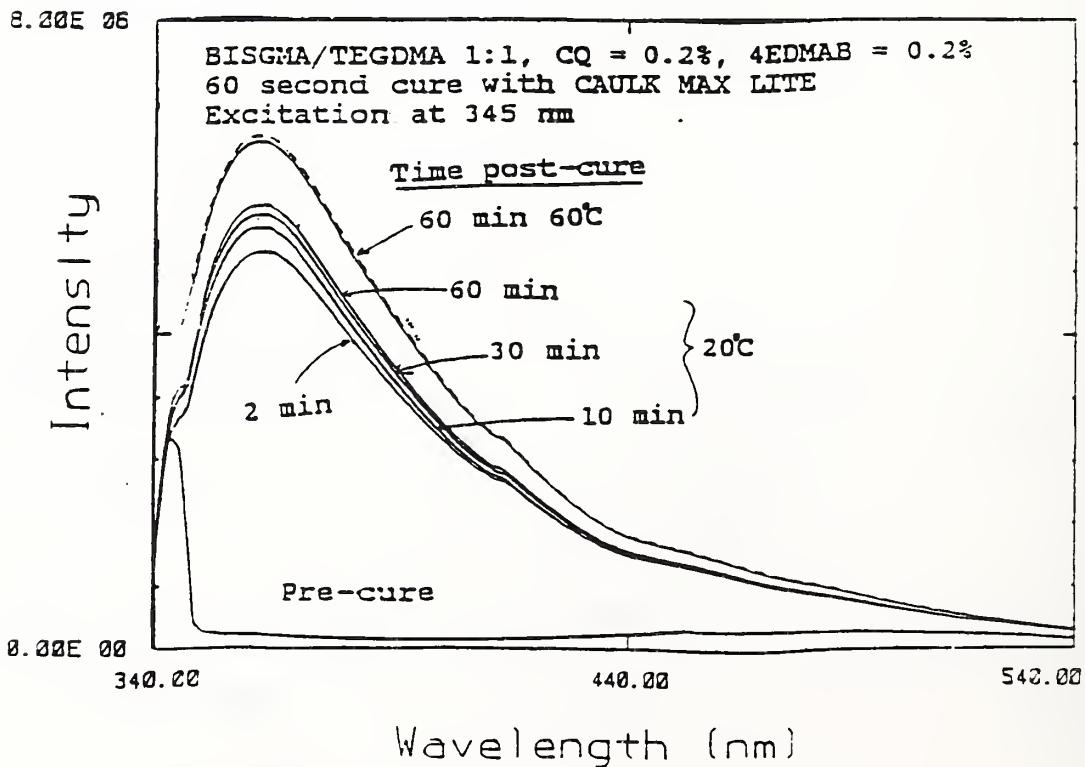


Fig. 4

## Excitation Spectrum of 4EDMAB with Cure

4.00E 05

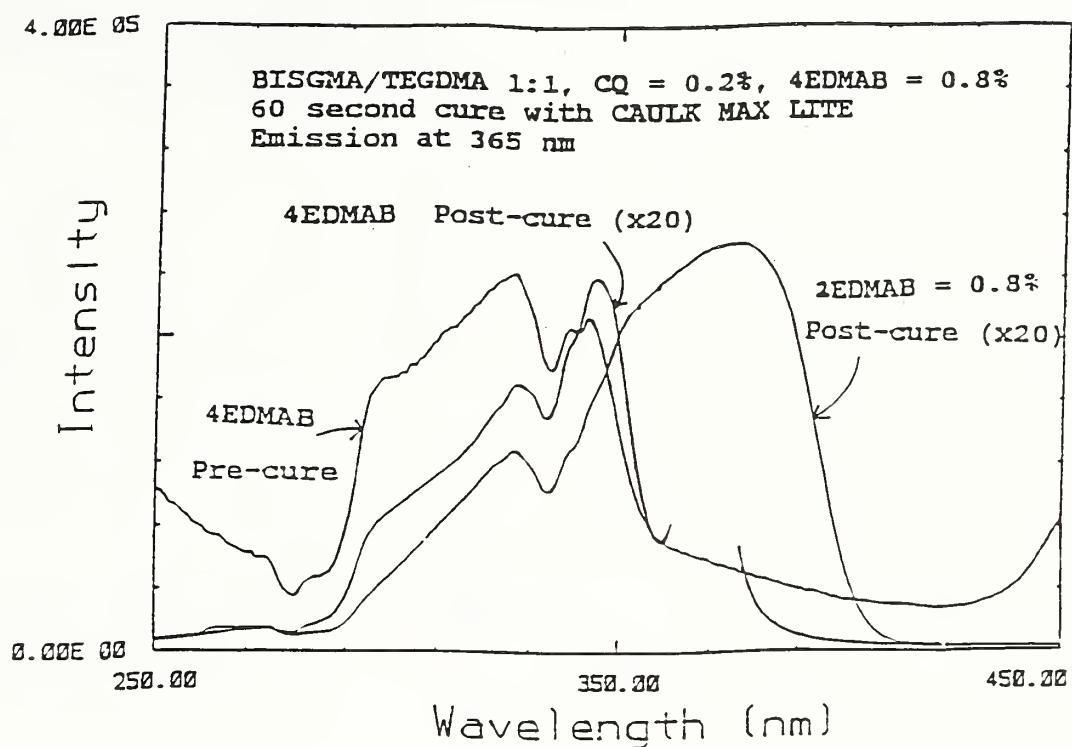


Fig. 5

## Fluorescence of 4EDMAB:

8.00E 06

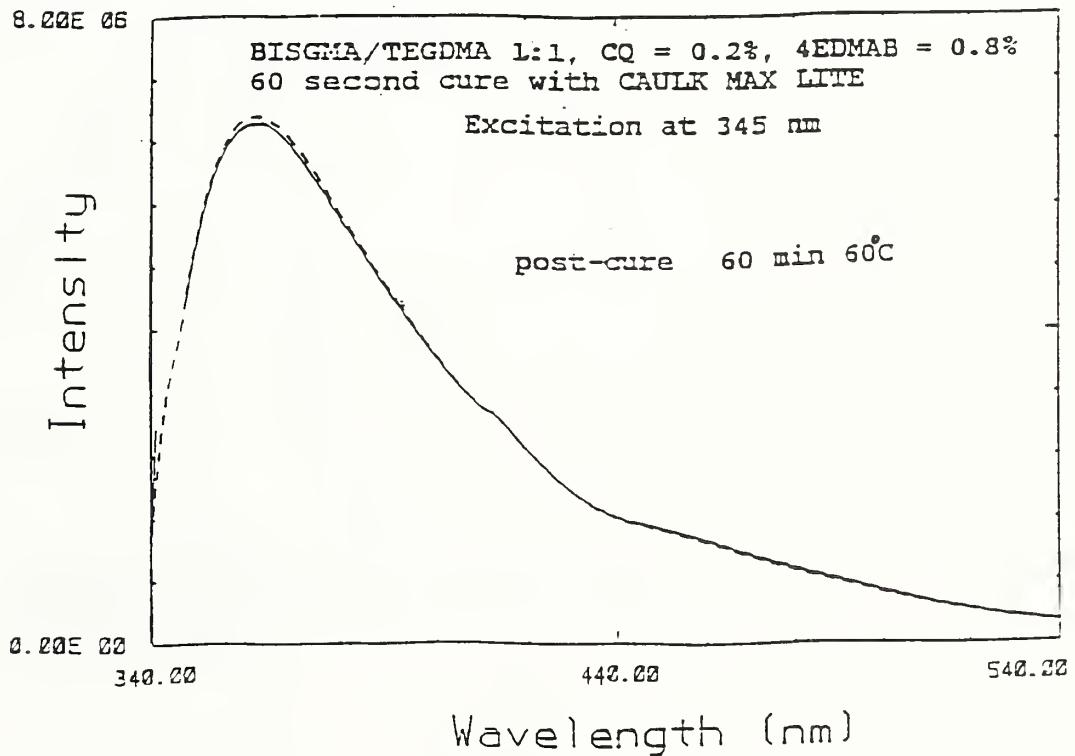


Fig. 6

## Excitation Spectrum of 2EDMAB with Cure

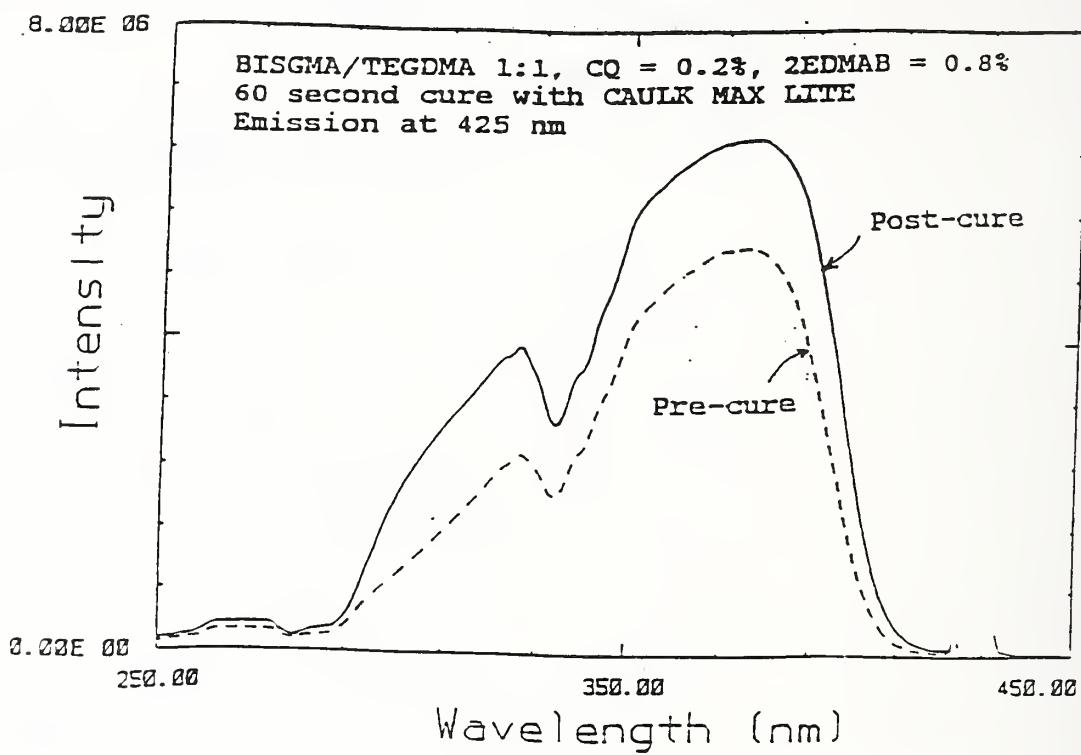


Fig. 7

## Fluorescence of 2EDMAB with Cure

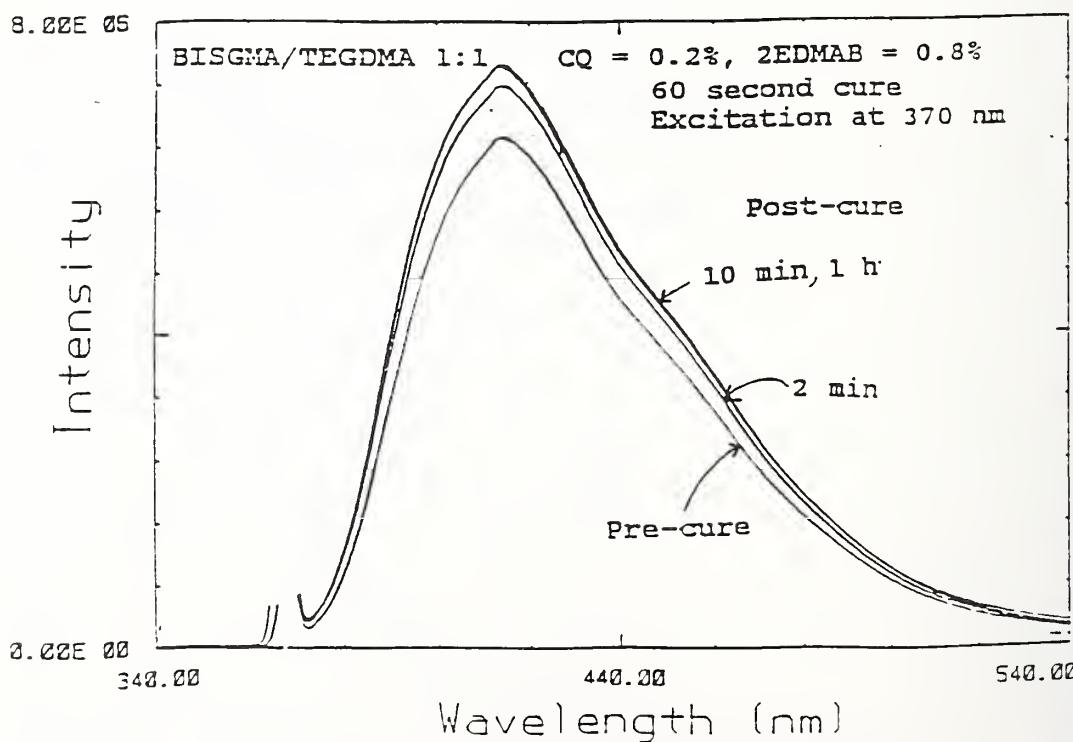


Fig. 8

## Excitation Spectrum of 3EDMAB with Cure

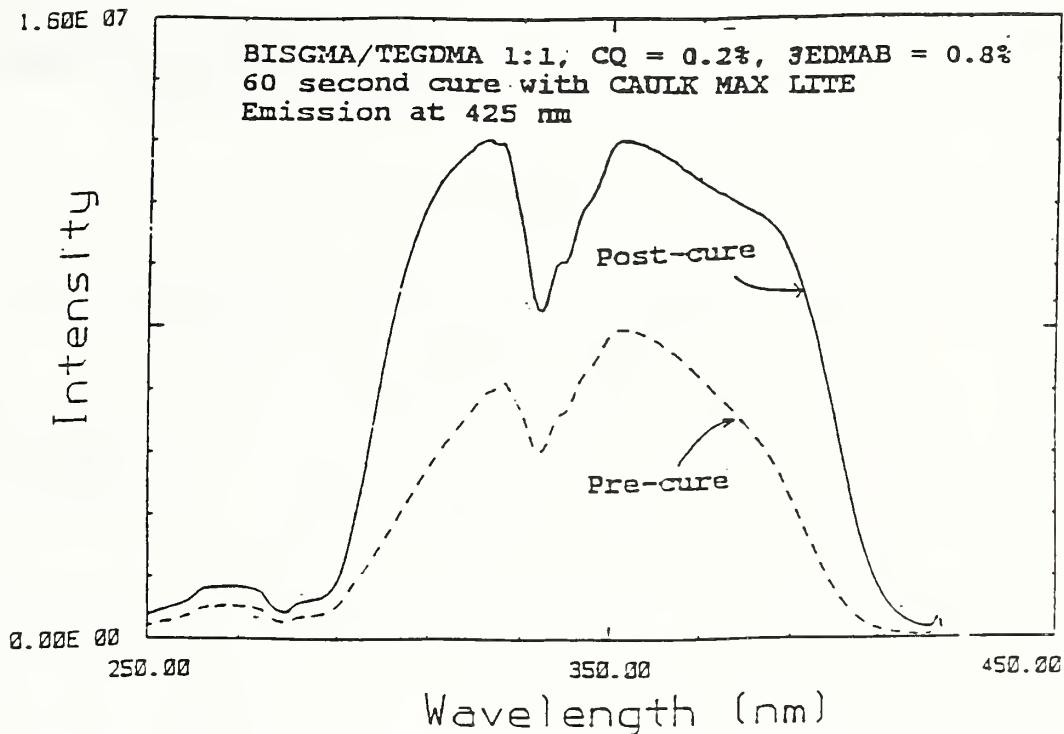


Fig. 9

## Fluorescence of 3EDMAB with Cure

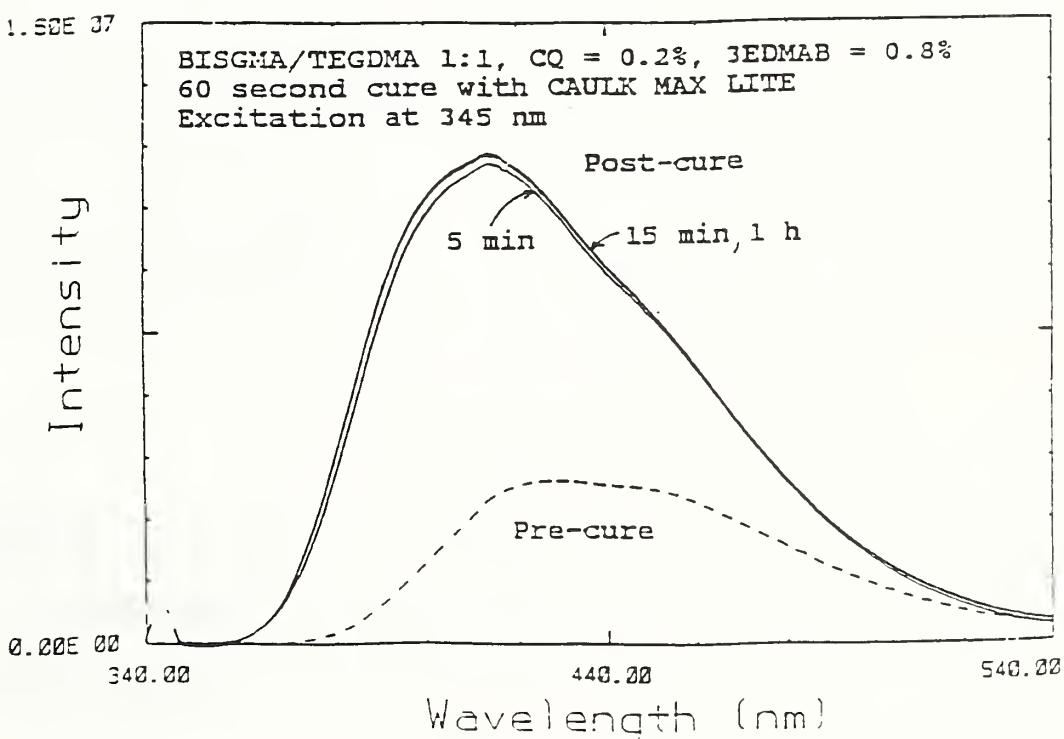


Fig. 10

## Excitation Spectrum of DMPT with Cure

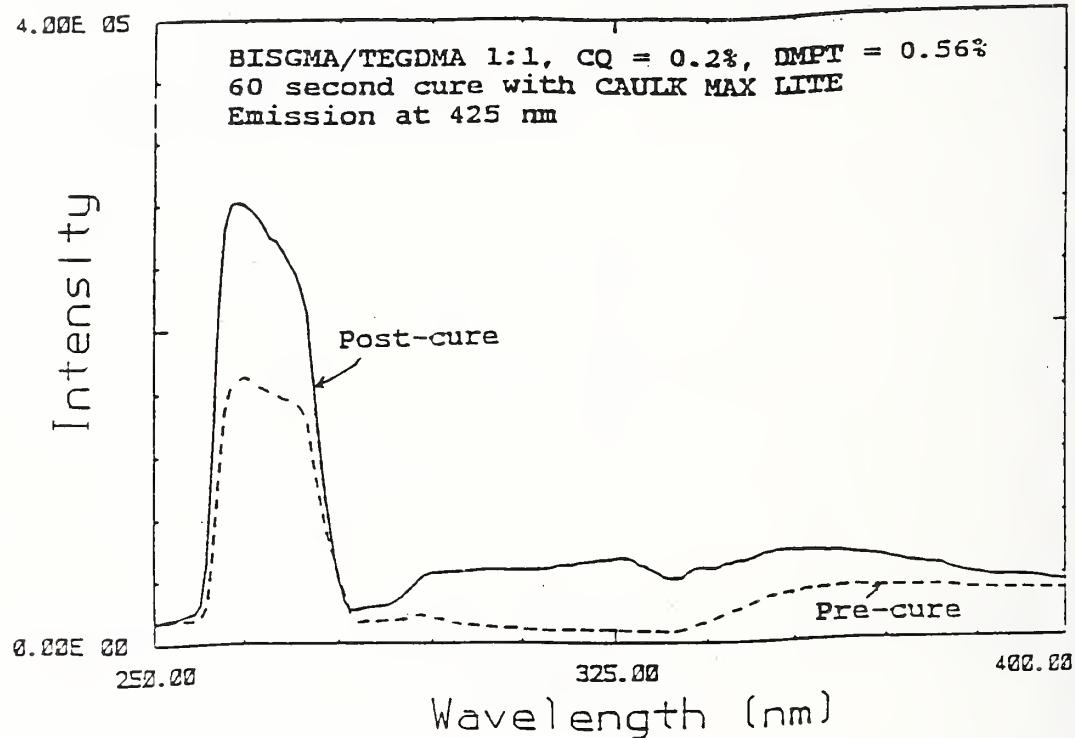


Fig. 11

## Fluorescence of DMPT with Cure

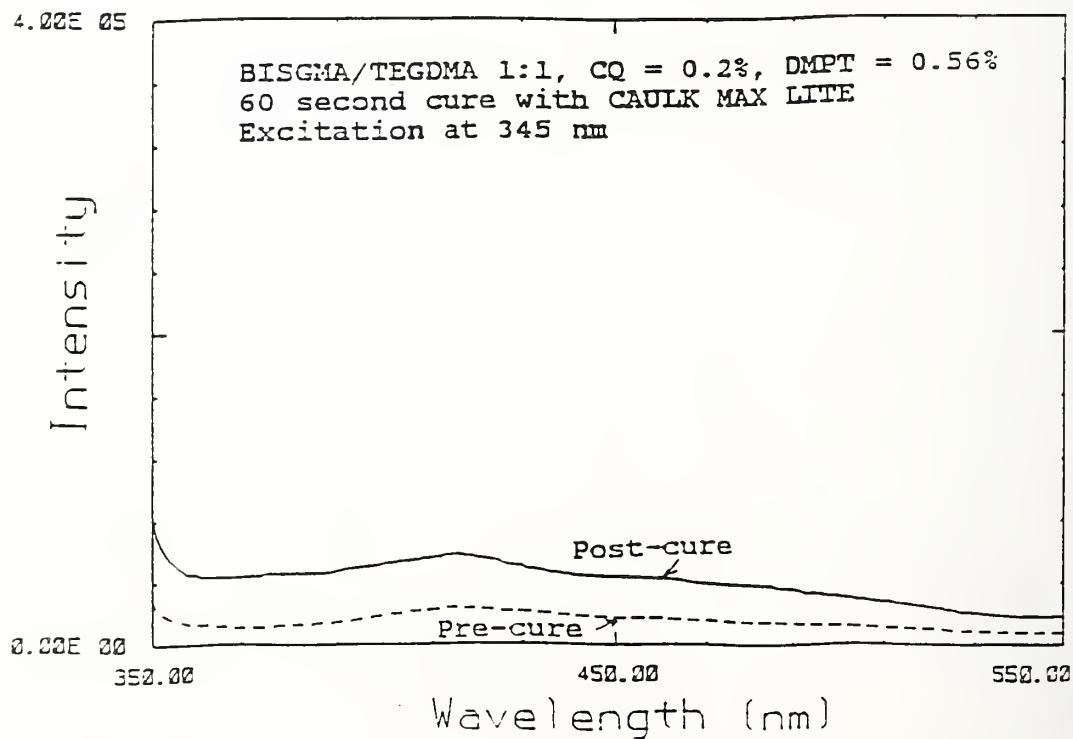


Fig. 12

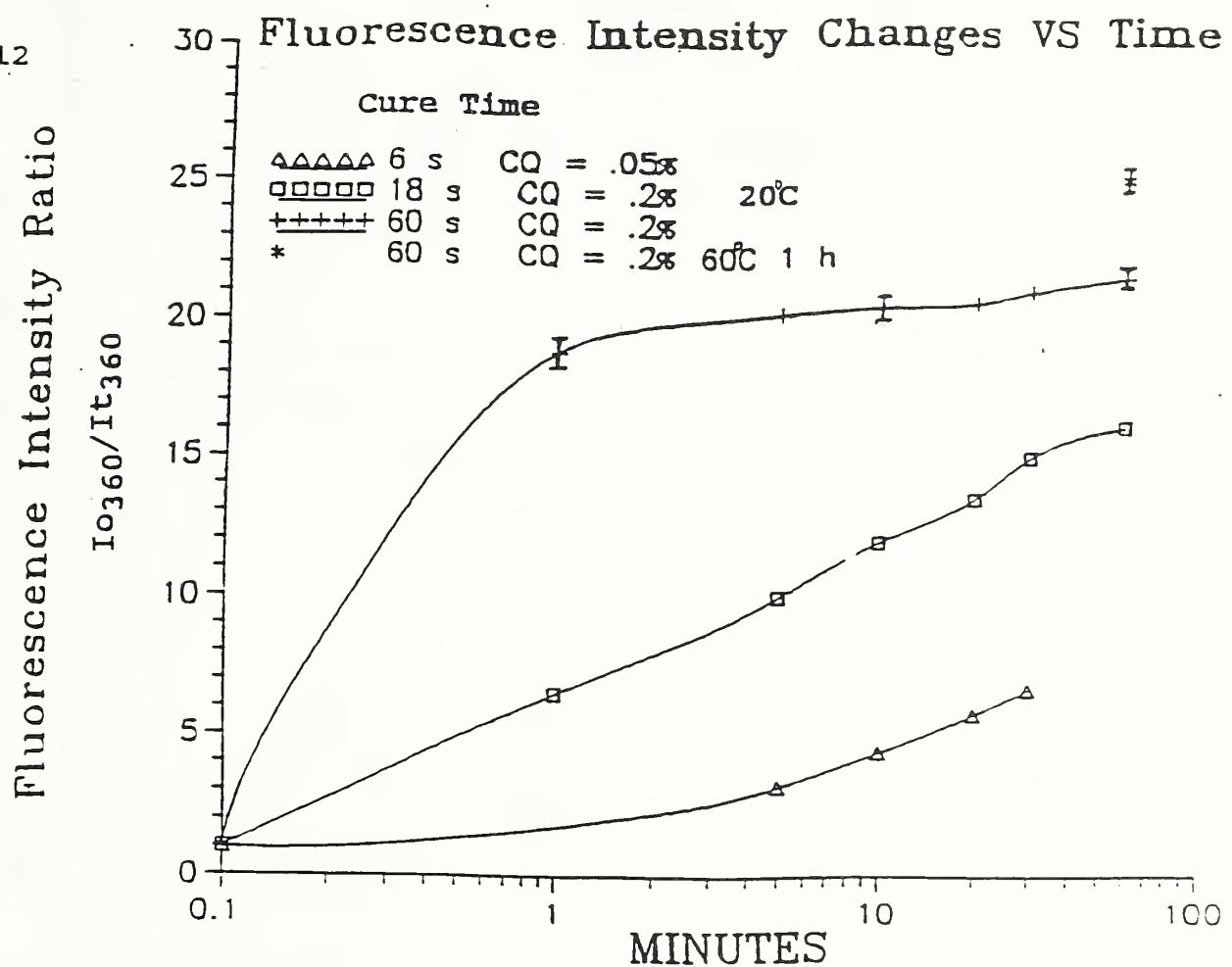


Fig. 13

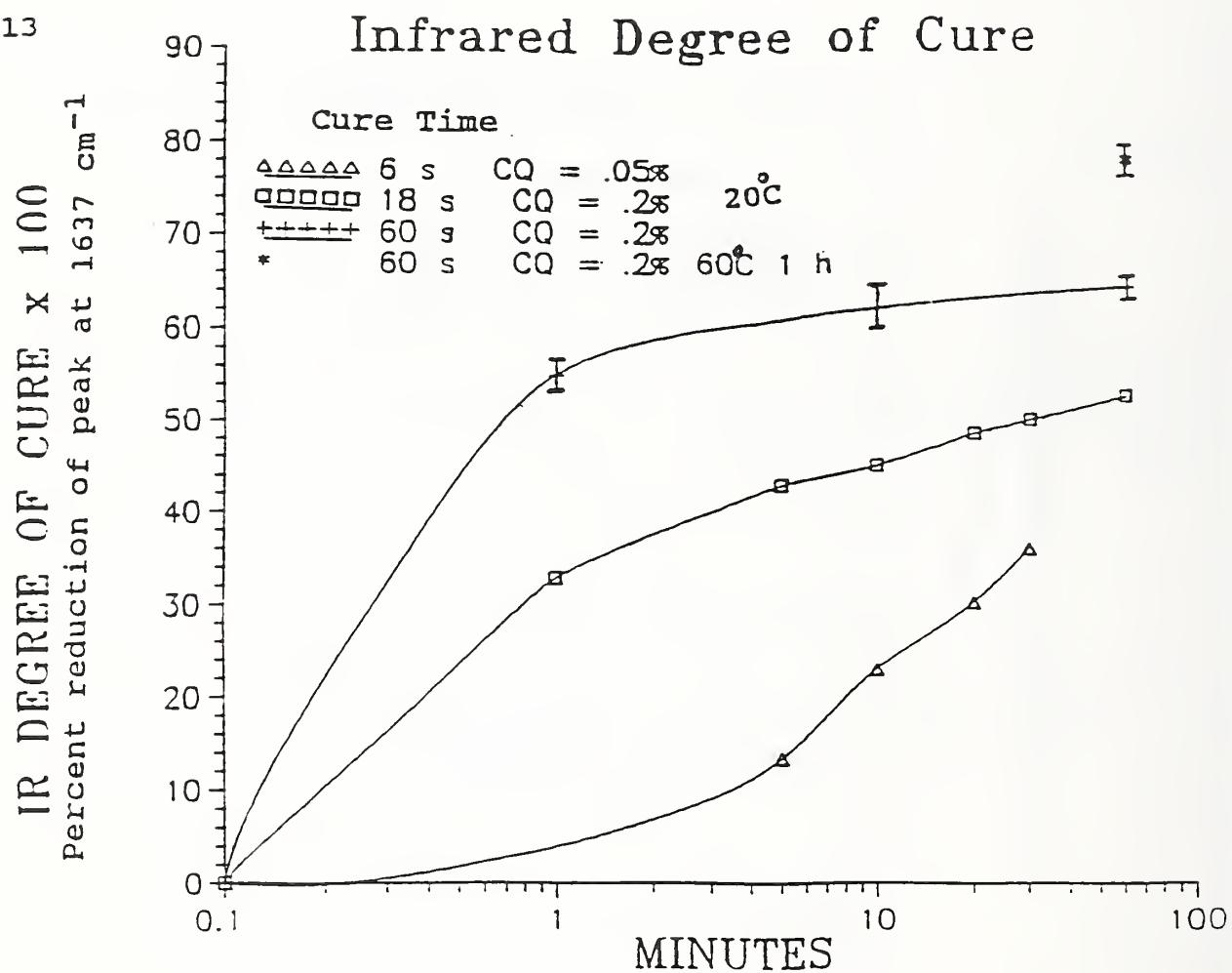
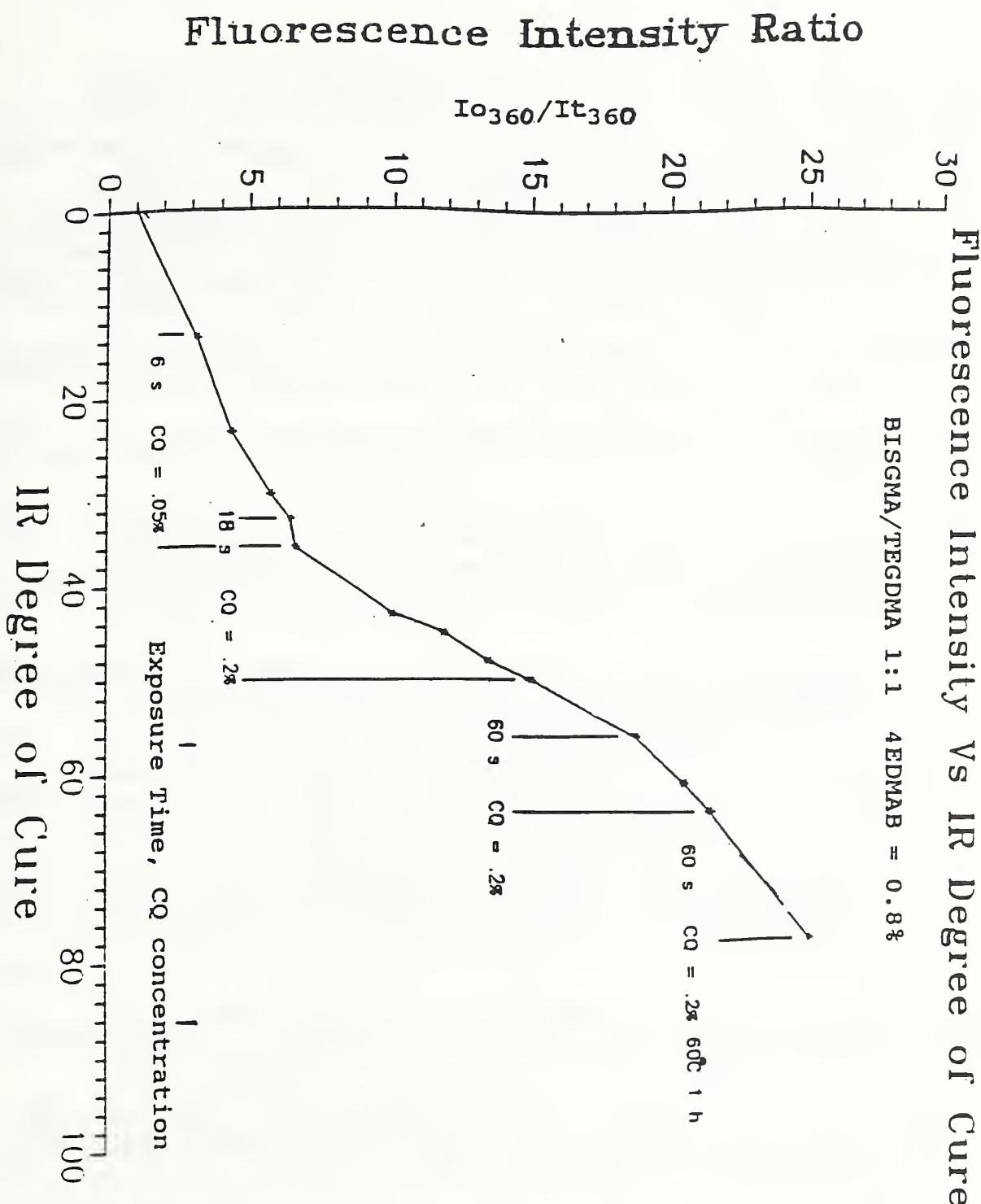


Fig. 14



Percent reduction of peak at  $1637\text{ cm}^{-1}$

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## PART II. Wear Resistance and Durability Assessment of Dental Composite Restoratives and Related Materials

### Overview

The general objective of conducting wear studies is to evaluate the durability of dental composite restoratives and related materials as an aid in the development of new resin formulations and model composite systems. For this work two classical pin and disc wear apparatuses can be employed: (1) a first generation unit, (NIST-1), which bathes specimens with flowing water and; (2) a second generation unit, (NIST-2), for which the bathing medium can be chosen from a variety of food simulating liquids (including water) with the capability for providing constant exposure of the specimen. A complete description of the mechanical aspects of the (NIST-1) wear machine has been previously described. [1] A description of the variables thought to be important in wear tribology, including the effects of pre-conditioning in solvents and acidic conditions, has been summarized in previous reports. [2,3,4] This project consists of the following phase:

Phase V This phase has two components:

- (A) Round-Robin Wear and Chemical Degradation Study of Posterior Composites
- (B) Complete Construction of the Modified Wear Testing Apparatus

Phases I, II, III, IV, and VI which had been part of the three year proposal have been incorporated into Part 1 of the proposal. They are no longer distinct projects but those activities on wear are conducted solely as needed in support of the work in Part 1.

- (A) Round-Robin Wear and Chemical Degradation Study of Posterior Composites.

### Background

The majority of our efforts in this reporting period involved participation in an ADA sponsored "round robin" wear and chemical degradation study designed to evaluate the wear of several commercial posterior composites on different types of wear machines at participating laboratories. Other mechanical tests that were performed were flexural strength, flexural modulus, polymerization shrinkage and solubility in water and in a 75% solution of ethanol in water. Participation in this study had two

primary objectives: 1) to provide researchers with an expanded data base which may be useful in the design and evaluation of future wear and degradation studies, and 2) to help NIST researchers understand how NIST wear and other related results compare with those from other laboratories.

#### PROGRESS REPORT

A major goal of this study was to measure the in vitro wear of several commercial dental composites using a three station pin-on-disk wear machine and compare the results with their flexural strengths. A complete description of the (NIST-1) wear device can be found elsewhere. [1] The composites used were Ful-Fil, Herculite XR, Heliomolar RO, Silux Plus, and an unsilanized material with a Ful-Fil type formulation. The composite disks were well-cured and stored in water for two weeks before testing as directed by the study protocol. The wear pin was a 2 mm diameter stainless steel rod with an average applied contact stress of 10 MPa. The wear results were made by measuring the average depth of the wear track with a linear variable differential transformer (LVDT) after 9600, and 40,000 revolutions. The average wear results (and S.D.) in micrometers at the end of the wear run were found to be: Ful-Fil = 24.5 (7.5), Heliomolar = 45.1 (4.1), Herculite = 60.5 (10.7), Silux = 67.9 (10.3), unsilanized material = 152.1 (47.1) (see Table 1 and Figure 1). The magnitude of the final wear results were analyzed using Bartlett's test of homogeneity of variances [5] which showed that the unsilanized material had a statistically higher ( $p < 0.05$ ) standard deviation than the other materials. A modified t-test showed that the unsilanized control also had significantly higher wear than the commercial materials. The wear means for the commercial materials were analyzed using a Newman-Keuls Multiple Comparison test ( $p < 0.05$ ), which ranked the in vitro pin-on-disk wear results as follows:

Ful-Fil < Heliomlar RO < Herculite XR = Silux Plus.

The results for Macor (a machinable glass ceramic material) which was intended as a low wear negative control showed that it wore catastrophically in our pin-on-disk apparatus with an average value of 888  $\mu\text{m}$  after 4000 revolutions (over 100 times faster than the commercial composite materials).

The unsilanized material wore considerably faster than any other commercial material, but the results showed much larger standard deviations. This may be due to the non-uniformity of the unsilanized material (many small air

bubbles were present as seen in the SEM photographs). In addition, the exfoliation of the unsilanized filler particles may have had an additional effect of producing three body wear with the loose filler particles acting as an abrasive. The track surface of the unsilanized sample also accumulated wear debris from the stainless steel pin faster than the other materials.

Ful-Fil exhibited the least amount of wear in these tests and appeared to be stained by the wear debris from the metal pin. Silux and Heliomolar, two microfilled composites, had highly polished wear tracks with no visible metallic stain or metallic wear debris. Herculite had intermediate staining.

It is interesting to note that the wear rates for Silux, Heliomolar and Herculite are nearly linear with revolutions (or time), whereas for Ful-Fil and the unsilanized material the wear rate decreased with time; the later two materials were also observed to have the most imbedded metallic wear debris which may have some shielding effect on the wear process. The wear of the opposing pin was measured on a few selected runs and found to be:

Material	N	Pin Length Loss	
		$\mu\text{m}$	(STD)
Unsilanized	6	340	(60)
Ful-Fil	6	380	(50)
Silux Plus	3	100	(30)
Heliomolar RO	3	100	(30)
Herculite XR	3	180	(30)

The wear on the opposing pin was found to be the lowest for Silux and for Heliomolar as might be expected for the micro-filled composites.

Flexural tests were conducted on composite samples after two storage conditions. To assess the effects of water storage on the degradation of the silane-filler bond, samples were kept in water at either 37 °C for 24 hours or 100 °C for 1 week prior to testing. The mean flexural strengths,  $\sigma$ , and flexural moduli,  $E$ , are shown in Table 2 and Figures 2 and 3. The Hybrid type commercial composites (ie. Ful-Fil and Herculite XR) had significantly higher strength and modulus values than the microfine composites (Heliomolar RO and Silux Plus). The unsilanized control was significantly weaker than the other materials.

Boiling the specimens for 1 week diminished the mechanical properties but the effect was surprisingly low. This observation would imply that the boiling procedure did not

catastrophically damage the silane-filler interfacial bonding. No general correlation could be made between the pin-on-disk wear values and flexural strengths for all the materials (i.e. Heliomolar was more wear resistant than Herculite even though it has a lower flexural strength). Comparing the flexural strength of Ful-Fil and the unsilanized control material with a similar formulation showed that silanization increased the strength four-fold.

An additional mechanical test to investigate the correlation between compressive mechanical properties and wear resistance was performed on the commercial materials used in the round robin study. The results are shown in Figures 4 and 5 for several different storage conditions and indicate that in compression, Herculite, Ful-Fil and Heliomolar (23 °C 10 days) have strengths between 330 and 360 MPa, whereas the strength of Silux is below 300 MPa. Time and post cure temperature increase the compressive modulus.

Another mechanical property investigated by both compression and flexural testing is the total work to fracture (the total area under the force vs displacement curve), the results of which are shown in Figures 6 and 7. Figure 6 indicates that for compression, the microfine materials have as good or better energy storage abilities as compared with the hybrid type composites. In the flexural testing mode, Ful-Fil and Herculite appear to be the toughest materials followed by Heliomolar then by Silux with the unsilanized material by far the worst (less than 10% the value of Ful-Fil).

Solubility of the composites was also tested in water and in 75% ethanol by immersing the cured disk samples for two weeks and then measuring the weight loss after desiccation. The results are shown in Figure 8. The unsilanized control lost the most weight (6  $\mu\text{g}/\text{mm}^3$  in water, and 26.8  $\mu\text{g}/\text{mm}^3$  in ethanol), while the other materials were less affected. Heliomolar was an exception, however, and lost 12.8  $\mu\text{g}/\text{mm}^3$  after ethanol immersion and severe surface crazing was also noted after three days of drying.

Polymerization shrinkage measurements were conducted using a mercury filled U-tube dilatometer, with a digital linear variable differential transducer (LVDT) to measure the changes in the height of the mercury meniscus. [6] This device was different from the one recommended in the round robin test protocol which utilized a water filled density bottle with a capillary tube for visual measurement of the

meniscus. The values of the polymerization shrinkage are seen in Figure 9 and are given in Table 3 below along with values compiled by Feilzer *et al.* [7] using a comparable device. The values at 1 hour are seen to be quite similar.

Table 3 Comparison of Shrinkage Measurements

Material:	NIST		Feilzer et al (1988)	
	1 hour	24 hour	1 hour	24 hour
	40 s cure	80 s cure	60 s cure	60 s cure
Unsilanized	4.46(.10)			
Ful-Fil	3.30(.10)		3.3 (.1)	4.2 (.1)
Silux	2.53(.13)	2.91(.18)	2.5 (.2)	3.4 (.3)
Heliomolar RO	2.44(.07)	2.57(.15)	2.1 (.1)	2.8 (.2)
Herculite	3.31(.07)	3.70(.13)	3.0 (.2)	3.6 (.3)

General conclusions of round robin testing

When the results of all the wear tests from the different laboratories were compared by normalizing to the fraction of the wear of the unsilanized material as seen in Figure 10 a large amount of variation is apparent and no general conclusions can be made about the wear machines at the different laboratories. Figure 11 shows the sum fraction of the wear from the different devices. This graph shows that when the wear data is combined, all of the materials are about the same, and they are all better than the unsilanized control material.

B. Complete Construction of the Modified Wear Testing Apparatus

Background

Over the past several years considerable activity was devoted to the design, acquisition of components and construction of a new version of the original (NIST-1) pin-on-disk wear machine. The advantages of the new device (NIST-2) are that it has more flexible computer control over the wear run parameters and a more reliable data acquisition system. The NIST-2 wear machine has independent stepper motors which allow for variable speed and more accurate positional control. Furthermore, the new design allows the specimen to be immersed in food simulating liquids, other than water, while the wear run is in progress.

## PROGRESS REPORT

Several design problems were encountered in the construction of the new wear machine that were corrected during this reporting period. Firstly, the stepper motors were previously found to be susceptible to resonance instabilities at the desired velocity of 27 rpm. Speed reduction gears and flexible belts were installed which allowed the motors to operate at four times the rotor speed, which is well above the motors natural resonance frequency. Secondly, it became evident that recirculating fluid jets would be needed to flush the wear debris from the surface of the wear specimens. These were added as well as a heater bath to maintain external temperature control, and a sub-micron filter was added to remove wear debris from the system.

After these modifications were implemented a brief study was conducted to assess the variability of the new wear machine and compare the wear rates with the results of the round robin wear study generated previously on the NIST-1 wear machine. The results are tabulated below Table 4.

Table 4 Wear rates from NIST-2 wear machine vs round robin values from NIST-1 wear machine

Material	Wear rates ( $\mu\text{m}/1000$ revolutions)			
	NIST-2 machine	N	NIST-1 machine	N
Ful-Fil	0.65 (.51)	6	0.61 (.18)	9
Heliomolar RO	1.16 (.12)	9	1.12 (.10)	9
Herculite XR	1.22 (.27)	6	1.51 (.26)	9
Silux Plus	1.72 (.31)	9	1.70 (.26)	9
unsilanized control	2.14 (.50)	5	3.80 (1.18)	9
Adaptic II	1.65 (.76)	12		
P-50	0.75 (.42)	8		
BIS-GMA/TEGDMA 7/3				
5/1 silanized glass	0.51 (.23)	12		
5/1 unsilanized	3.09 (.30)	3		

In comparing the wear rate between the two machines it is clear that the values for the micro-fine materials (Heliomolar and Silux) are almost identical in both magnitude and standard deviation. Although the value for Ful-Fil is similar in magnitude the standard deviation has increased sharply with the NIST-2 machine. Herculite and the unsilanized material have slightly lower wear rates on the NIST-2 machine. The effect of silanization is quite evident when looking at the values of an experimental composite formulation of BIS-GMA/TEGDMA resin mixture with 5 parts of corning 7724 glass, with and without A-174

silane treatment. In this case the unsilanized material wore six times as fast as the silanized formulation.

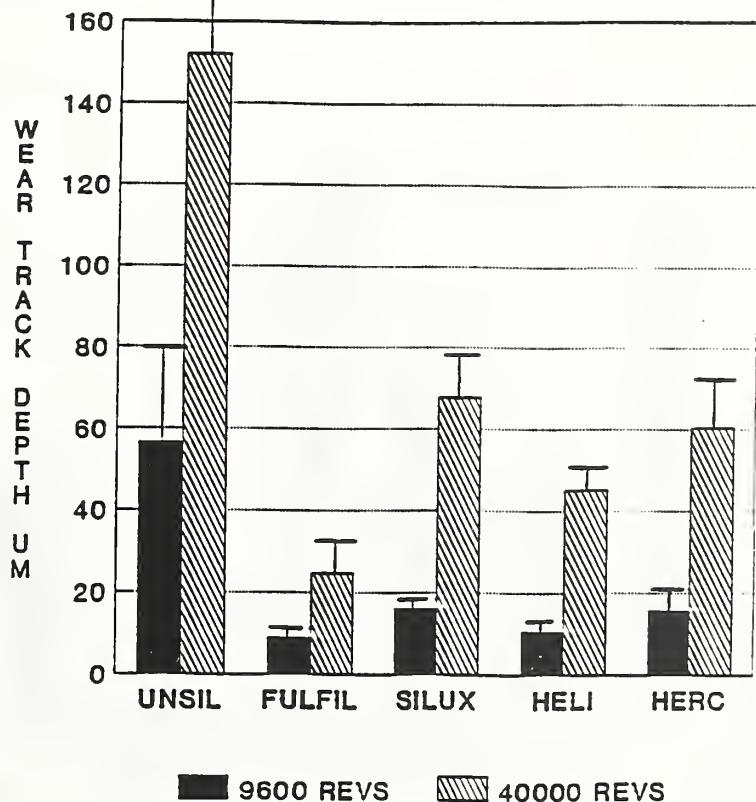
Table 1

## NIST PIN-ON-DISK WEAR MACHINE

WEAR TESTING SUMMARY SHEETS			
Wear Test Material	N=	Initial Mean Wear Results: $\mu\text{m}$	Final Mean Wear Results: $\mu\text{m}$
Unsilanated Composite #26990 (L.D. Caulk)	9	56.6 (25.1)	152.1 (47.1)
Silux Plus (3M)	9	16.0 (2.4)	67.9 (10.3)
Herculite XR (Kerr)	9	15.7 (5.9)	60.5 (10.7)
Heliomolar (Ivoclar)	9	10.6 (2.5)	45.1 (4.1)
Fulfil (L.D. Caulk)	9	8.9 (2.8)	24.5 (7.5)
Macor (Corning)	8	174.5 (165)	888.3 (335)

1. Wear Test Measurement System: Depth of wear track (LVDT) in  $\mu\text{m}$
2. Initial Measurements at 9600 revs 24% (~6 hours) \*
3. Final Measurements at 40,000 revs 100% (~24 hours) \*
- \* 4. Measurements for Macor are at 1/10 the time for composite material (i.e. 960 revs and 4,000 revs)

FIGURE 1

WEAR TEST RESULTS  
NIST PIN-ON-DISK

■ 9600 REV S      ■ 40000 REV S

•MACOR DATA OFF SCALE (WEAR RATE APPROX. 100 TIMES)

Table II

## Effect of Storage Conditions on Composite Flexural Properties

MATERIAL	STORAGE CONDITION	Flexural Strength $\sigma$ MPa	Flexural Modulus E MPa (S.D.)
UNSSLANIZED	24 HOUR 1 WEEK BOIL	31.4 (3.0) 26.5 (3.1)	5,790 (170) 4,990 (235)
FUL-FIL	24 HOUR 1 WEEK BOIL	132.2 (9.9) 108.3 (13.1)	10,250 (160) 9,510 (310)
SILUX	24 HOUR 1 WEEK BOIL	61.7 (2.3) 49.6 (2.8)	6,740 (200) 6,340 (110)
HELIOMOLAR	24 HOUR 1 WEEK BOIL	90.2 (3.6) 82.8 (7.8)	6,290 (90) 6,436 (80)
HERCULITE	24 HOUR 1 WEEK BOIL	130.4 (20.1) 120.9 (19.4)	12,000 (210) 10,380 (420)

Fig. 2

## FLEXURAL STRENGTH

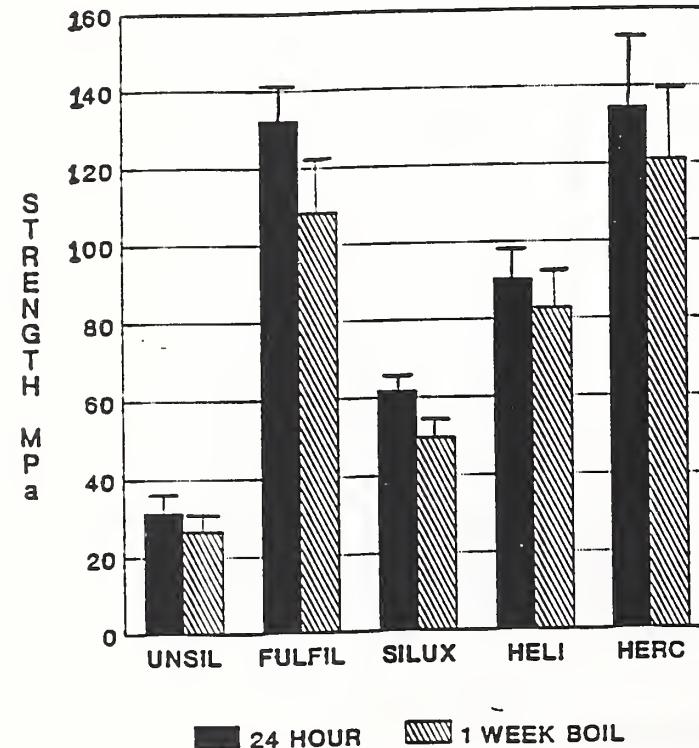


Fig. 3

## FLEXURAL MODULUS

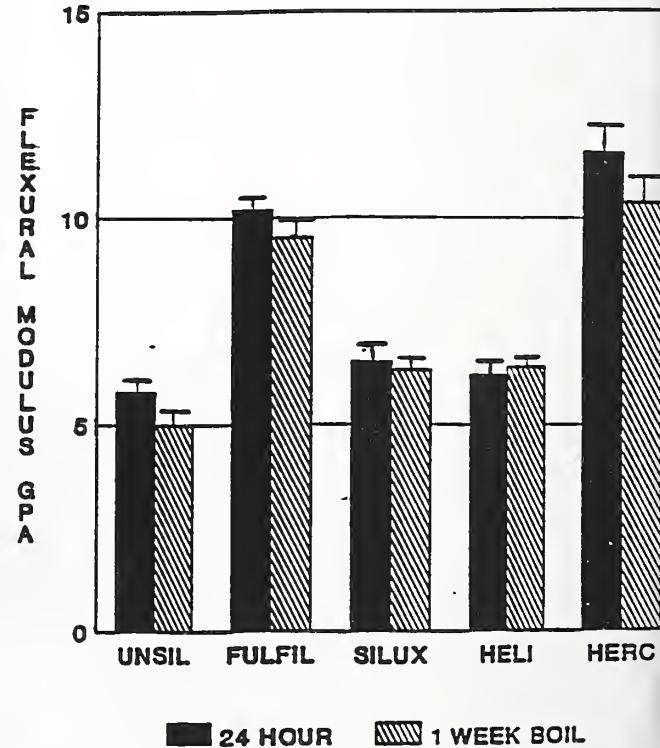


Fig. 5

## COMPRESSIVE MODULUS

COMMERCIAL AND EXPERIMENTAL COMPOSITES

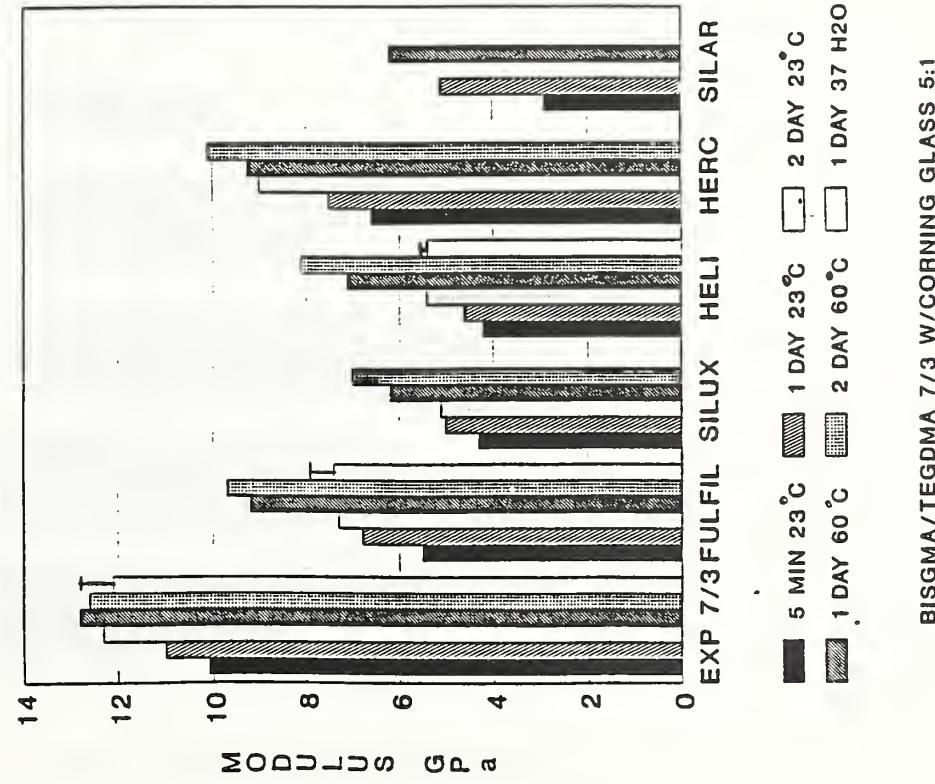


Fig. 6  
STORED ENERGY AT FRACTURE  
Compression (KN X MM )

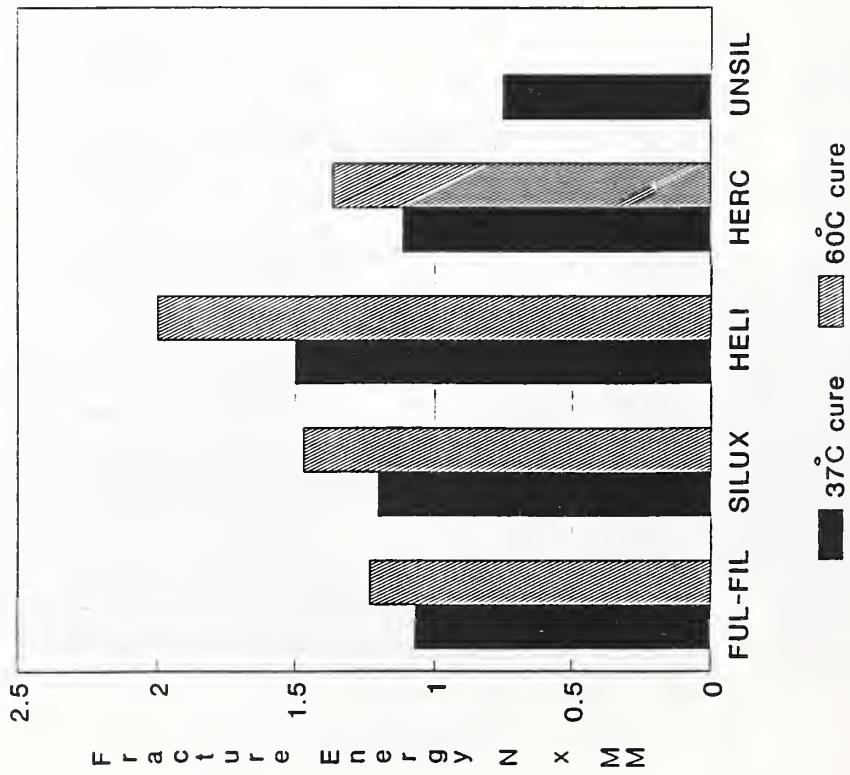


Fig. 7  
STORED ENERGY AT FRACTURE  
Flexural (N X MM )

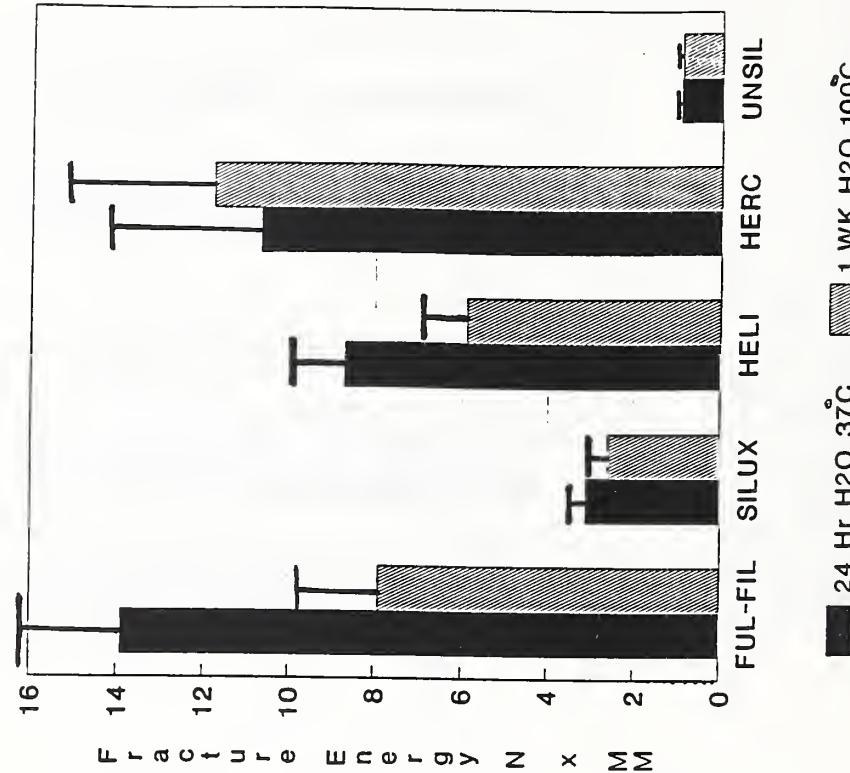


Fig. 8

## SOLUBILITY RESULTS

ugram/mm<sup>3</sup>

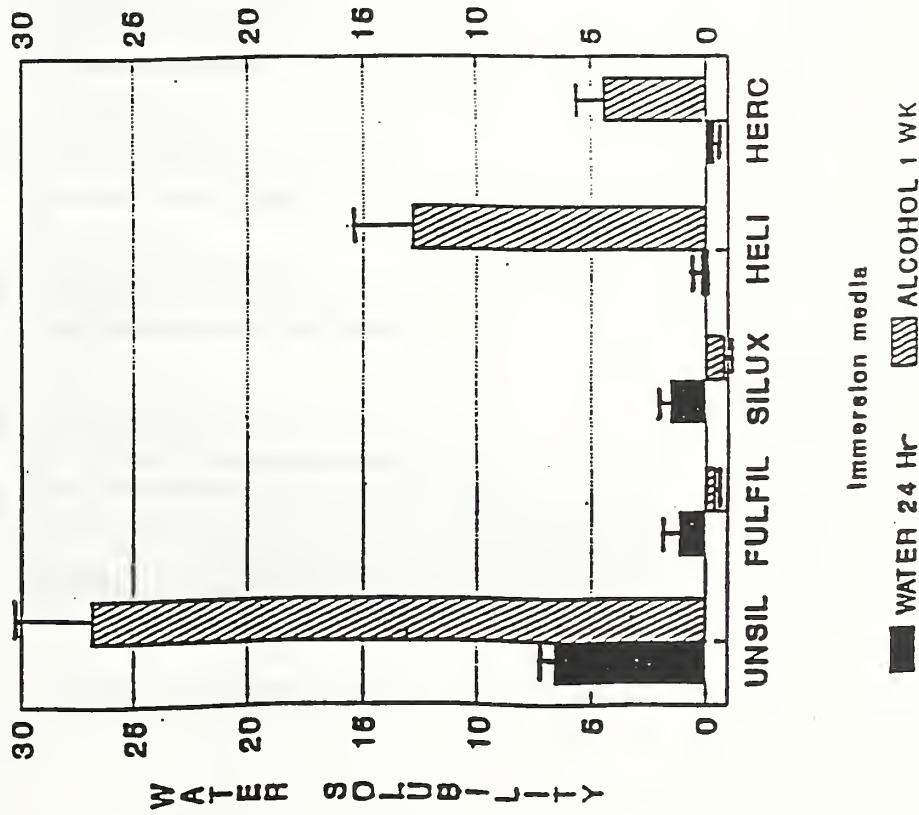


Fig. 9

## SHRINKAGE RESULTS (1H)

MERCURY U-TUBE DILATOMETER 25°C

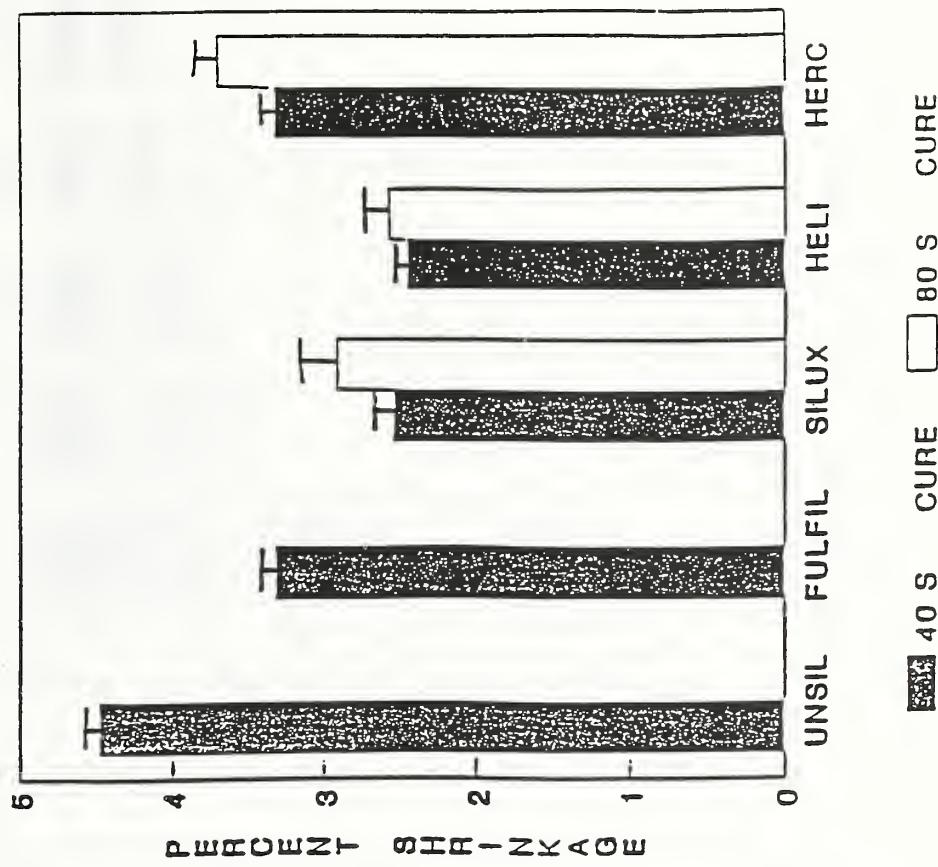
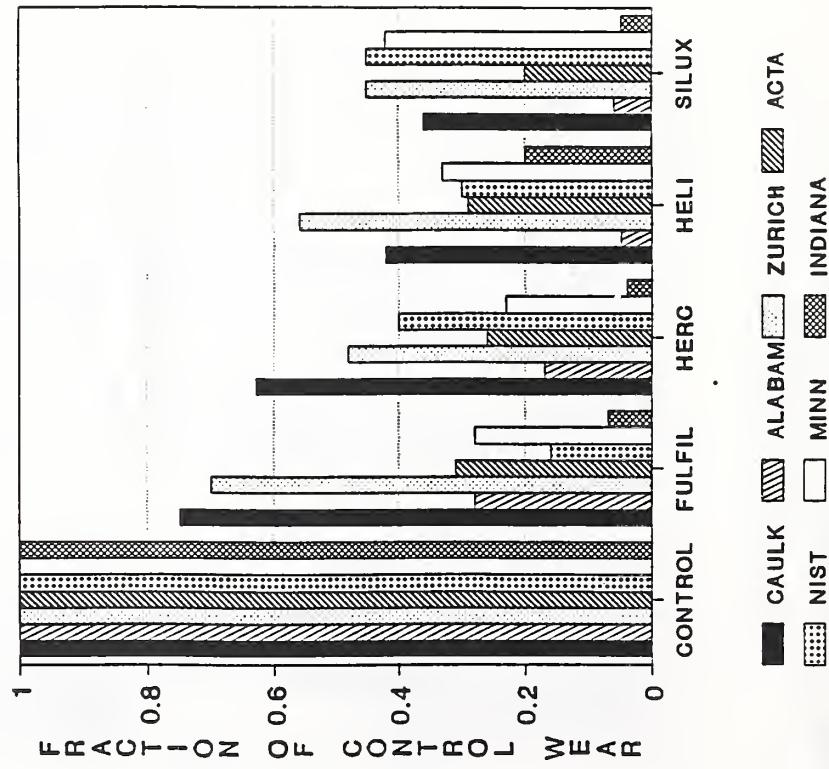


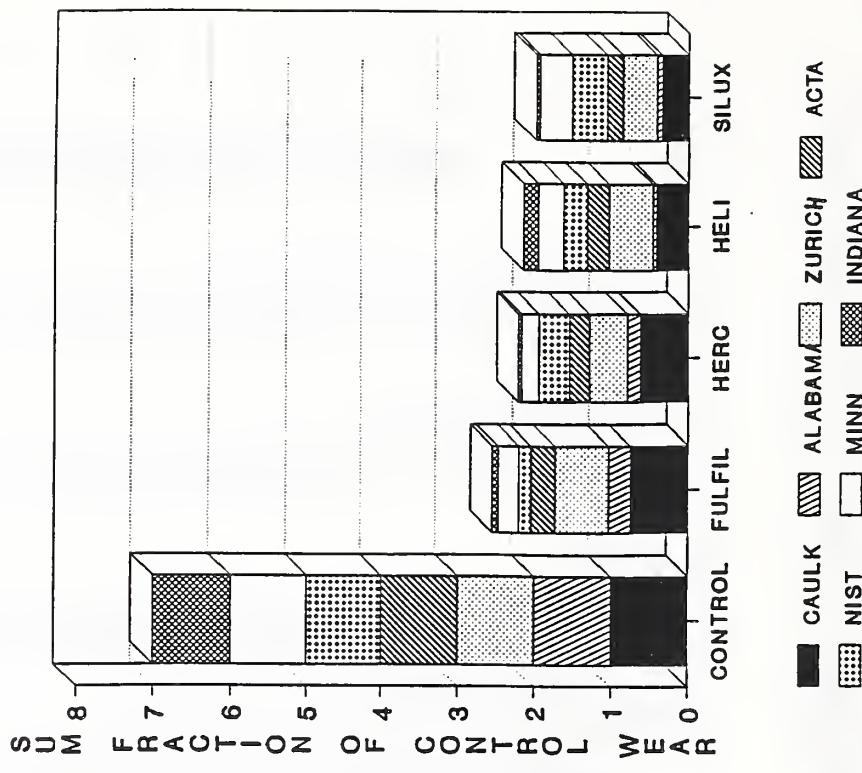
Fig. 10  
NORMALIZED WEAR VALUES  
Linear against control composite



ALL VALUES TAKEN AT 100 % WEAR TIME

Fig. 11

NORMALIZED WEAR VALUES  
Linear against control composite



ALL VALUES TAKEN AT 100 % WEAR TIME

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## PART III. Dental Alloys, Ceramics, Metrology and Analyses

### Overview

Porcelain fused-to-metal (PFM) restorations constitute a major type of dental prosthesis. Wide fluctuations in the costs of dental restorative precious metal alloys have ensued over the past ten years. At the same time new materials for fabrication of non-metallic restorations have been introduced as have alloys of various kinds for cast metal restorations. The new materials can vary considerably in their fabrication characteristics and clinical performance. Although failure rates of PFM restorations are low, ~ 1-2% in the first year [1] and 2-3% over 7 to 10 years [1,2], the costs associated with each failure are high. More reliable methods than now exist are needed to evaluate properties and develop methods to aid in improvement of clinical performance. For porcelain fused-to-metal alloys the prime factors include thermal-stress compatibility, porcelain-metal system strength, alloy castability and the attendant capability of producing good fitting castings. Metrology plays an important role as the significance and relevance of materials properties needs to be more fully addressed in terms of relationships to clinical performance, reliability and predictability. Any measurement technique or process that can affect material properties or interpretation of clinical data rightfully belongs in this category.

In summary, this part focuses on dental alloy and ceramic systems and the use of Weibull statistics and finite element stress analysis for the determination of the strengths and origins of failure in bonded (and other) dental restorative systems.

The prospects for commercialization of gas plasma sterilization are summarized here as a completed, discontinued project. It was concluded that the ability to sterilize under specific conditions was feasible; however, the costs of the components required for a commercial unit were considered too high by the collaborating American company for a successful new product. Furthermore, the initially perceived advantage of faster sterilization was negated by the recent introduction of faster steam sterilization units.

A. **Stress in Prosthetic and Restorative Systems, (Porcelain-Metal Thermo-mechanical Compatibility)**

**PROGRESS REPORT**

Overview

Residual and transient stresses in porcelain metal systems are considered to be major factors which influence their fabrication and service reliability. Compressive surface stresses may make restorations less prone to failure; tensile surface stresses and large interfacial stresses (body-opaque, opaque-metal) are considered less desirable. The geometries of porcelain-metal restorations are complex and influence the stresses developed from either fabrication and/or mastication etc.

New material systems, fabrication techniques, and restorative designs continue to be introduced. As the introduction of new materials and designs proceeds, it is desirable to have clearer understandings of how transient and residual stresses are developed, and how major material and fabrication factors can affect their magnitudes. Thus, the design of systems and fabrication methods can be more effectively guided by engineering principles and, when failures occur, they can be more readily interpreted. This study was undertaken to delineate effects of material properties, geometry (thickness) and fabrication (cooling-heating) variables on the development of thermo-mechanical stresses.

Accomplishments

The viscoelastic and elastic properties of several dental porcelains and alloys have been used in viscoelastic models of porcelain slabs and porcelain-metal slabs to calculate the development of both transient stresses and residual stresses [3,4]. The factors included in the calculations were: Temperature dependent shear viscosities of porcelains [5,6], temperature dependent coefficients of thermal expansion of alloys and porcelains [4,7,8], temperature dependent elastic moduli [9], cooling rate dependence of glass transition temperatures (porcelain) [10], cooling rate dependent temperature distributions, several cooling rates, and several thicknesses.

Our modeling [4] has resulted in empirical equations which can describe interfacial and surface stresses as functions of cooling rates and specimen thicknesses. Our more recent calculations have revealed several interesting aspects of viscoelastic behavior of dental porcelain

related to porcelain-metal compatibility [11]. At the deformation temperature,  $T_d$ , which depends on the heating rate of porcelain,  $q$ , and the stress applied,  $\sigma_o$ , a stress  $\sigma$  develops which is dependent on the coefficient of thermal expansion of the porcelain,  $\alpha$ , and the difference in coefficients of thermal expansion between the porcelain and the metal substrate;  $\Delta\alpha = \alpha_p - \alpha_m$ . The relationship found is  $\sigma_o/\sigma = \alpha/\Delta\alpha$  eq.1. For ordinary commercial porcelains and alloys used for dental metal-ceramics, Asaoka and Tesk [11] reported that the instantaneous  $\alpha$  at the deformation point of the porcelain is  $30 \sim 40 \times 10^{-6}/^\circ\text{C}$  and instantaneous  $\Delta\alpha = (30 \sim 40 \times 10^{-6})/^\circ\text{C} - (15 \sim 17 \times 10^{-6})/^\circ\text{C} = 13 \sim 25 \times 10^{-6}/^\circ\text{C}$ , respectively leading to approximate values of

$$\sigma_o/\sigma \sim 1.2 \text{ to } 3.1 \quad \text{eq.1}$$

If  $T_d$  is the temperature at which a stress of 1 MPa develops in the porcelain during the cooling of PFM strips,  $T_d$  should be determined for the same porcelain with a load on the push-rod of the dilatometer which produces ( $\sim 1.2 - 3.1$ ) MPa during heating. It was also shown [9] that the deformation temperature,  $T_d$ , is related to the activation energy  $Q$ , the applied stress,  $\sigma_o$ , the coefficient of thermal expansion,  $\alpha$ , and the shear viscosity constant,  $\eta_o$ , as:

$$T_d = (Q/R) \ln(\sigma_o/q \cdot \alpha \cdot \eta_o) \quad \text{eq.2}$$

where  $R$  is the universal gas constant.

In accordance with the above discussion, the activation energy for viscosity,  $Q$ , and the viscosity constant,  $\eta_o$ , can be calculated from determination of  $T_d$  from expansion curves of the porcelain with loads greater than  $1.2 \sim 3.1$  MPa under a constant heating rate. When properties as shown in Table 1 are used, load bearing temperatures,  $T_b$ , and deformation temperatures,  $T_d$ , are as shown in tables 2 and 3 respectively. The values of  $T_d$  in table 3 are calculated with the use of equation 2 and the simulations. All of the temperatures calculated here are in good agreement. When the applied stress is under 1 MPa,  $T_d$  occurs at temperatures higher than  $630^\circ\text{C}$ . The temperature where  $\eta/E$  ( $E$  is the Young's modulus) becomes less than 1.0 s is over  $640^\circ\text{C}$ . The exact value of  $T_d$  is difficult to measure because of the low viscosity of the porcelain, as discussed for  $T_b$  in Table 2. Eq. (2) shows that  $T_d$  increases by only  $4^\circ\text{C}$  when the coefficient of thermal expansion at  $T_d$  is increased from  $30 \times 10^{-6}$  to  $40 \times 10^{-6}/^\circ\text{C}$ . The heating rate also affects  $T_d$ ; the increase in  $T_d$  when

the heating rate is increased from 1°C/s to 50°C/s is about 50°C.

Eq. 2 was derived from equating the creep rate to the thermal expansion rate at  $T_d$ ; i.e.,  $\alpha/\eta = \alpha \cdot q$  eq. 3  
 From eq. 3:  $\alpha \cdot q = \alpha_0/\eta$ , then  $\alpha = \alpha_0/\eta \neq \alpha_0 \cdot q/\eta$  eq. 4

Hence,  $\alpha$  may be determined from measurement of  $T_d$  at a given heating rate,  $q$ , with an applied stress  $\sigma_0$  and determinations of  $\eta$  by other methods.

The load-bearing temperature,  $T_b$ , is the point at which the net negative deformation of the specimen above  $T_d$  is 2%. It is possible to calculate  $T_b$  from the following equation:

$$\int_{T_R}^{T_b} \alpha(T) dT + \int_{T_R}^{T_b} \frac{\sigma_0 dT}{q\eta_0 \exp(Q/RT)} = -0.02 \quad \text{eq. 5}$$

where the first term represents the amount the specimen would expand in the absence of both externally applied forces and surface tension, and the second term represents the creep strain rate due to a compressive stress (defined as negative) at any temperature,  $T$ , integrated over the temperature range with a heating rate of  $q$ . The sum of these two must, by definition be -0.02. The second term has no exact integral, but by making the substitution  $u = Q/RT$  and using the following relation [12] it can be calculated numerically.

$$\int_u^{\infty} e^{-u} U^{-b} dU = U^{1-b} e^{-u} \sum_{n=0}^{\infty} \frac{(-1)^n (b)^n}{U^{n+1}} \quad \text{eq. 6}$$

Table 2 shows measured values of  $T_b$  by Oda et al. [13],  $T_b$  calculated from Eq. 5, and  $T_b$  determined from simulations. Here, the heating rate is 0.5 °C/s. The simulations were conducted two ways using the Maxwell model and one of two conditions: (1) The slab maintained a stress distribution when the porcelain was at high temperature and had low

viscosity, or (2) uniform stress when  $\eta/E$  of the porcelain became less than  $\Delta T/q$  (the relaxation time of the porcelain). The two simulations and calculated results are in good agreement with the experimental data.

Experimental data with stresses of 2 and 10 MPa are close to the range of the results from the simulations made with the two different assumptions. This is discussed in the next paragraph.

$T_d$  becomes imprecisely determined when the applied stress is under 1 MPa. This is because internal stresses generated during heating are of this magnitude, and the deformation rate at any point is  $\epsilon = (\sigma_0 \pm \sigma_T)/\eta$ , depending on the sign of  $\sigma_T$ , where  $\sigma_0$  is the applied stress and  $\sigma_T$  is the thermal stress. In order for the overall deformation of the specimen to be controlled by the applied stress, the lowest value of applied stress must be greater than  $\sigma_T$ . From an elastic stress calculation based on the temperature distribution in a slab of 2-mm thickness, the surface of the specimen has about 1 MPa compressive stress during heating at a constant rate of 1 °C/s. When the heating rate is 10 °C/s, the surface of the same slab has a calculated compressive stress of about 10 MPa. Therefore, the stress which is caused by the temperature distribution in the slab is significantly higher than the applied stress under ordinary conditions for measurement of thermal expansion by use of a push-rod dilatometer. Under these conditions, the relationship between  $T_d$  and the externally applied stress loses its significance, and simulations and calculations are imprecise.

Table 1  
THERMO-MECHANICAL PROPERTIES OF THE PORCELAIN USED IN THE SIMULATION

Elastic modulus (a)	70.2 GPa at 30°C
Thermal expansion coefficient (b)	
$T < T_g$	$\alpha = (1.3 + 0.020 \cdot T) \times 10^{-6}/^\circ\text{C}$
$T > T_g$	$\alpha = \{\alpha' + 0.28(T - T_g)\} \times 10^{-6}/^\circ\text{C}$
	Here, $\alpha'$ is the coefficient at $T_g$
Liquid	$\alpha = 35 \times 10^{-6}/^\circ\text{C}$
Transition temperature (c)	460°C at 0.17°C/s
Viscosity (c)	$\eta = 3.6 \times 10^9 \exp(40400/T) \text{ Pa} \cdot \text{s}$

(a) Käse et al. (1985), (b) Asaoka, experimental results,  
(c) Bertolotti and Shelby (1979).

Table 2  
MEASURED AND CALCULATED LOAD-BEARING TEMPERATURE,  $T_b$  °C

Applied Stress (MPa)	Experiment		Results	
	1st firing	3rd firing	Calculated by Eq. (6)	Simulated Results
2	659	699	709	660-711*
10	660	669	672	660-674*
50	638	638	639	640
100	630	638	625	624

\*Lower and upper values are simulated results under assumptions (1) and (2), respectively, in the text.

Table 3  
SIMULATED AND CALCULATED DEFORMATION TEMPERATURE,  $T_d$  °C

Applied Stress (MPa)	Results Calculated by Eq. (20)	Simulated Results
2	627	628
10	595	595
50	566	568
100	554	555

A manuscript on the preceding results entitled "Viscoelastic Deformation of Dental Porcelain and Porcelain-Metal Compatibility" has been published [11]. The validity of the model simulations has been checked by comparing them with calculated deformation temperatures and by comparing simulated and calculated load bearing temperatures with experimental measurements. The results were reported in [11] and in NIST-IR 4566. Agreements were very good, to within a few degrees celsius.

#### Phase I

For the viscoelastic models of porcelain and porcelain-metal slabs developed for ceramic-metal systems during the previous term of the interagency agreement: vary the coefficients of thermal expansion,  $\alpha_1$ ,  $\alpha_2$ , and  $\alpha_3$  of metal, opaque and body porcelains, respectively, to determine how stresses change at the porcelain-body surface, body-opaque interface and opaque-metal interface. Each  $\alpha$  will be varied from a low to high value while holding the others constant. Other effects such as body, opaque and metal thicknesses, porcelain viscosities and activation energies

will also be explored. Other geometry models such as shells or cylinders will be considered.

#### PROGRESS REPORT

Work is now proceeding toward the development of more complex, shell-like models which are expected to provide better insight into the stresses in ceramic and ceramic-metal restorations. In order to accomplish this, use will be made of the Abacus finite-element program which the Polymers Division has on an Iris work station. Pre- and post-processing is expected to use a NISA-II program, which will be installed on a 3086 PC with 25 MHz capability.

The variations of parameters with the one dimensional model which has been used thus far proceeded with the acceptance of two preprints for the proceedings of the 3rd International Conference on Residual Stress, held July 23 to 26 in Tokushima, Japan. The first preprint [10] dealt with the effects of the coefficients of thermal expansion of dental body and opaque porcelains, in the glass transition temperature region, on residual stresses in porcelain metal systems which were simulated as undergoing Newton cooling. (We have found, experimentally, that Newton cooling is a good approximation to the cooling of porcelain disks.) According to Newton cooling, the temperature  $T$  is given by:  $T - T_0 = (T_i - T_0) e^{-mt}$ , where  $T_i$  = the initial temperature,  $T_0$  = the ambient temperature and  $m$  is a constant which relates the cooling rate,  $q$ , to any time  $t$ . For slow cooling,  $m = .03$  (almost furnace cooling), the effects of the coefficient of thermal expansion are shown in Figs. 1, 2, and 3.

For the computer simulations a PFM beam was modeled as composed of a metal substrate, 0.5 mm thick covered on one side with an intermediate 0.2 mm layer of opaque porcelain and an outer 0.8 mm layer of body porcelain. The porcelain component was modeled as composed of 50 thin layers of equal thickness; the metal was modeled as one elastic layer, homogeneous in temperature as the metal conducts heat much more rapidly than the porcelain. During cooling, each layer acquires its own unique temperature and the properties, such as coefficient of thermal expansion, Young's modulus, viscosity etc., characteristic of that temperature. Cooling is through one degree centigrade steps from a heat soak temperature. Elastic stresses are developed during each temperature step and these partially relax, depending on the cooling rate, until ambient temperature is reached throughout the beam as described in detail by Asaoka and Tesk [4]. For

the particular simulations conducted, Newtonian cooling was assumed with the surface temperature,  $T$ , of the beam changing as:

$$T = T_0 + A \exp(-mt) \quad \text{with } A = T_s - T_0 \quad \text{eq. 7}$$

where  $T_0$  is the ambient temperature,  $T_s$  is the ( $800^\circ\text{C}$ ) heat soak temperature, and  $m = 0.03$ . The constant,  $m$ , is from experimental determinations of the cooling of thin porcelain disks. For each porcelain, the coefficients of thermal expansion for the simulations were represented as follows:

$$\alpha = C_1 + C_2 T \quad T \leq T_{g \text{ onset}} \quad \text{eq. 8}$$

$$\alpha = \alpha(T_{g \text{ onset}}) + C_3(T - T_{g \text{ onset}}) \quad T_{g \text{ onset}} \leq T \leq T_{g \text{ finish}} \quad \text{eq. 9}$$

$$\alpha = C_4 = 35 \times 10^{-6} \quad T \geq T_{g \text{ finish}} \quad \text{eq. 10}$$

where  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_4$  are unique constants for each porcelain in its applicable temperature ranges and where  $\alpha(T_{g \text{ onset}})$  is the thermal coefficient of expansion at the onset of its glass transition temperature,  $T_g$ . After  $\alpha$  reaches  $35 \times 10^{-6}$ , as taken from experimental data for  $\alpha$  above the  $T_g$  range for that porcelain,  $\alpha$  is treated as a constant. The coefficient of thermal expansion of the metal was represented by a form of Eq. 2 throughout the entire temperature range as the metal does not have a  $T_g$ .

For the simulations, first the constant  $C_3$  for the body porcelain was varied while all other properties were held constant (Fig. 1). The value of  $C_3$  for the opaque porcelain was then varied, with all other properties of materials held constant (Fig. 2). Finally, the value of  $C_3$  for opaque porcelain was lowered to  $50 \times 10^{-9}$  from the value of  $75 \times 10^{-9}$  used for Fig. 1, and stresses were calculated for two different values of  $C_3$  for the body porcelain (Fig. 3).

The results of the simulations are shown in Figs. 1, 2 and 3. Fig. 1 shows that as  $C_3$  of the body is increased, the system tends more to a compressive stress within the surface of the porcelain; for the particular  $C_3$  for the opaque and for the  $\alpha$  of the metal considered, very little normal surface compressive stress can be generated.

If the opaque  $C_3$  is dropped to  $50 \times 10^{-9}$ , (Fig. 3) the trend is similar, but higher compressive surface stresses are developed, with higher values of  $C_{3 \text{ body}}$ . Examination of Fig. 2 confirms that higher values of opaque  $C_3$  are more desirable for lowering surface tensile stresses; however,

the tremendous effects of higher opaque  $C_3$  on producing tensile stresses at the opaque-body and opaque-metal interfaces should be noted. Such conditions might be detrimental to the survival of a prosthesis as the addition of tensile stresses from functional loads might lead to fracture at an opaque interface.

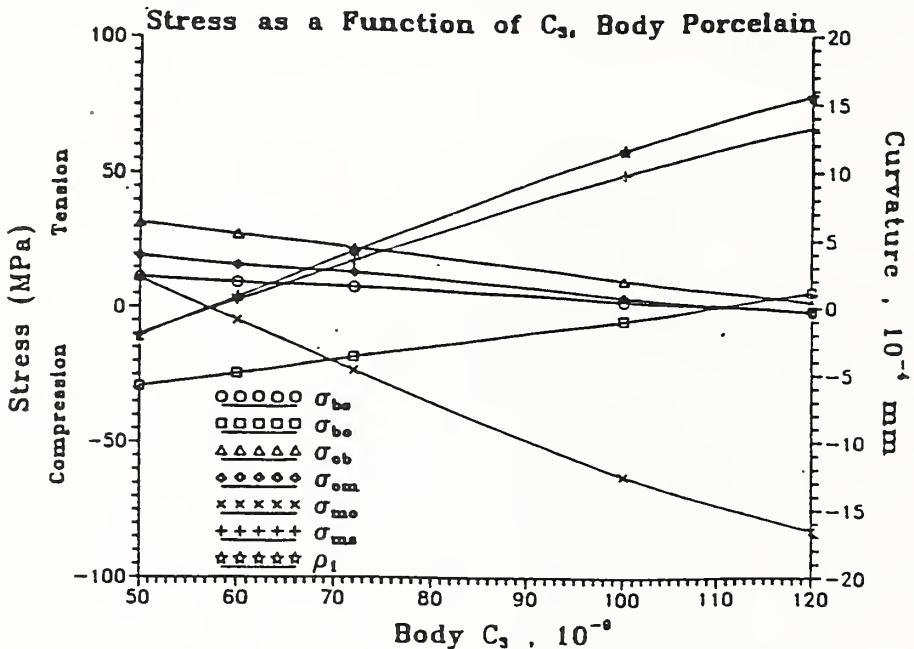


Fig. 1 Variations in  $C_3$ , body, while holding fixed: body;  
 $C_1 = 85.3 \times 10^{-7}$ ,  $C_2 = 11 \times 10^{-6}$ , opaque;  $C_1 = 76.8 \times 10^{-7}$ ,  
 $C_2 = 16 \times 10^{-9}$ ,  $C_4 = 35 \times 10^{-8}$ ,  $C_3 = 75 \times 10^{-9}$ . Stresses,  $\sigma$ , are:  
 $\sigma_{bs} = \sigma$  in body at surface;  $\sigma_{bo} = \sigma$  in body at body opaque  
interface;  $\sigma_{oo} = \sigma$  in opaque at opaque body interface, etc.

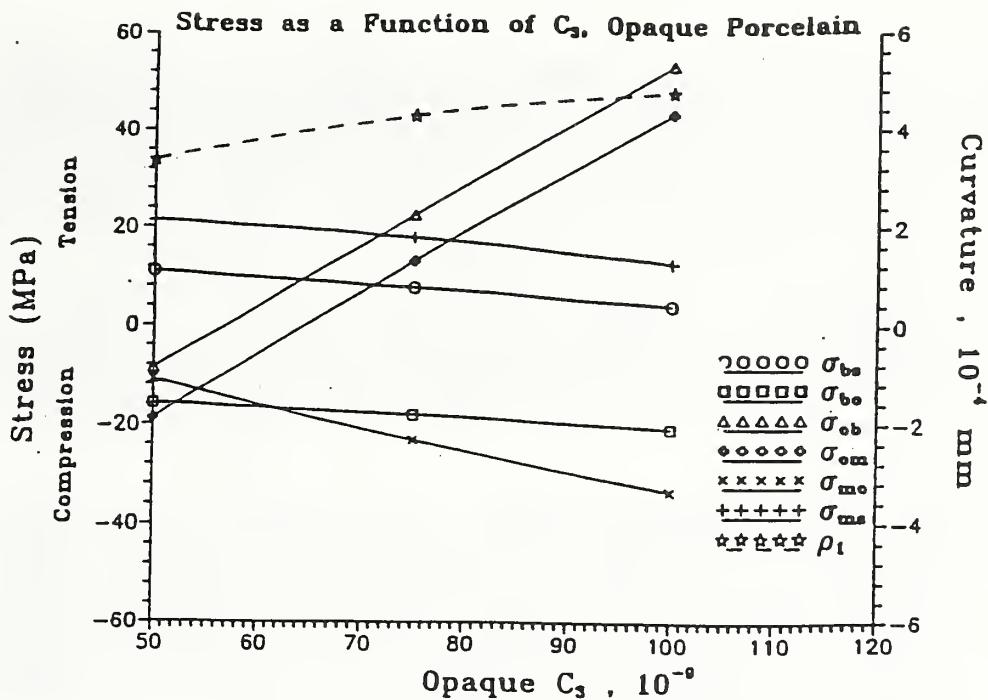


Fig. 2. Variation in  $C_3$ , opaque, with: body;  $C_3 = 72 \times 10^{-9}$ , all other  $C$ 's held as in Fig. 1.

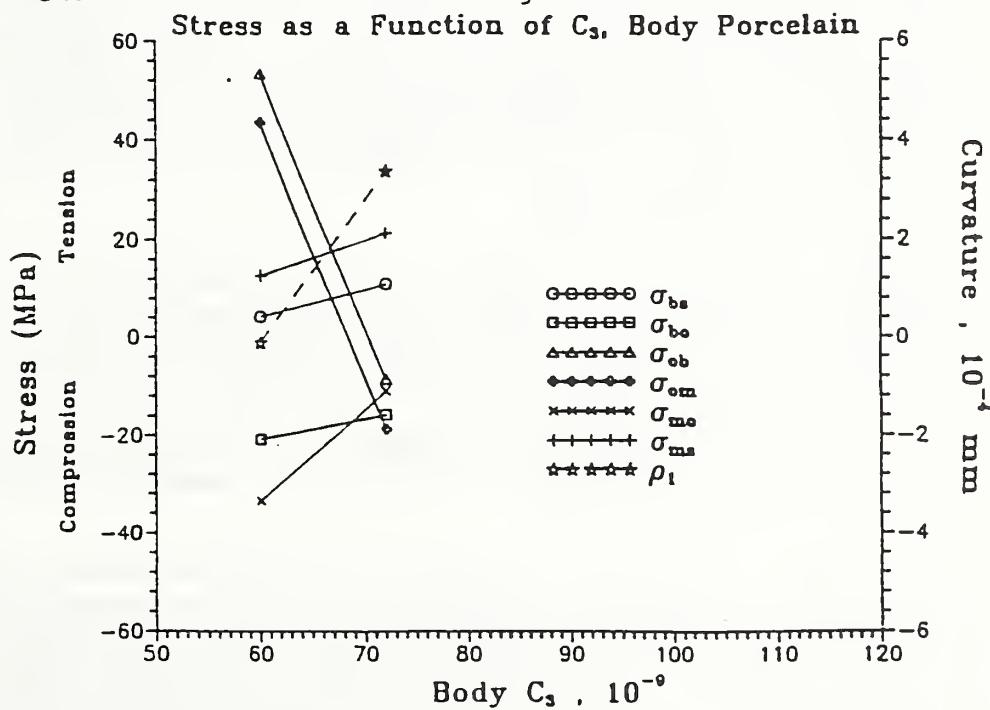


Fig. 3. Variation in  $C_3$ , body, but with  $C_3$ , opaque =  $50 \times 10^{-9}$ , rather than  $75 \times 10^{-9}$  as in Fig. 1.

The simulations conducted show that the sharper the glass transition temperature range is for the body porcelain of a PFM strip, the greater the tendency toward compressive residual stresses in the surface layer. However, due to the asymmetry of the strip modeled, the choice of the sharpness of the glass transition region for the opaque is a very important consideration for determining the sign and the magnitude of the stresses at the opaque layer interfaces and within the opaque layer. A judicious balance is required and points to a need for stringent product control of the coefficients of thermal expansion of the opaque porcelain within the glass transition region.

There are several aspects to the study which should be discussed. Foremost, the use of a beam model allows flexure stresses to be developed. In general, this flexure acts in such a way as to minimize the overall stress within the system. The development of flexure is thought to more closely mimic the conditions which pertain to partial porcelain coverage of connector-pontic sections or of the gingival collars of a crown.

Crowns and other sections which receive full porcelain coverage behave more like shells and are thus more rigid. This shell-like behavior should result in higher stresses overall than the present calculations show, but just which stresses will be raised, partially at the expense of others, should also be explored to more completely understand the effects of thermal expansion within the glass transition range. This will be the object of an extension of this work.

Another point to consider is that changing of the glass transition region while holding the temperature dependence of the shear viscosity constant is an artifact which may be expected to overestimate the effects of broadening of the glass transition range. Hence, the effects presented are expected to be upper bounds of effects in a PFM beam which allows flexure; the trends are expected to be the same but not as strong.

The many interrelated effects of coefficients of thermal expansion, sharpness of glass transition temperature ranges and asymmetry of PFM restorations have been shown to be complex. Qualitative reasoning is not liable to provide more than rudimentary notions of PFM potential reliability. Computer simulations via two dimensional finite element analysis of the multifaceted aspects are important for broadening the understanding for possible improvements in overall system designs. While the absolute magnitudes of the simulated results are not to be

taken so seriously, the effects of changes in variables on changes in the overall stress states can be enlightening. Both beam and shell-like simulations are progressing over ranges of variables for more complete understanding and, hopefully, for design of more durable systems.

#### Phase II

After one complete series of Phase I simulations at one cooling rate, additional simulations will be run with the cooling rate as the variable.

#### PROGRESS REPORT

This work is underway. The Newton cooling approximation is being extended from  $m = 0.03$  to  $m = 0.83$ . This approximates cooling with an air blast to produce tempered specimens.

#### Phase III

Development of charts, figures and empirical formulae, etc. which will depict the effects of  $\alpha$ 's cooling rates, etc.

#### PROGRESS REPORT

This is proceeding, coincident with the results obtained in Phases I and II (see Figs. 1, 2, 3) .

#### Phase IV

Calculation of stress relaxations at fixed temperatures or for chosen temperature ramps as functions of the holding and cooling conditions. Vary the relative porcelain viscosities to determine trends which can be useful in the design of more desirable stress-state systems.

This Phase will be pursued following the investigations in Phases I and II.

#### Phase V

For alloy systems which undergo phase transformations, develop models which incorporate the effects of phase transformations into viscoelastic calculations of stress as affected by such transformations under a variety of cooling regimens.

## PROGRESS REPORT

In order to aid the understanding of these effects, we conducted computer simulations of stresses developed in a PFM strip. Pd alloys were chosen as Pd-based alloys form the basis for some major alternatives to high cost gold alloys, yet can maintain many of the desirable characteristics. The Pd-Cu alloy system which has a super lattice at 40.3 atomic % Cu displays a typical first-order transformation feature. The transient stresses in the porcelains and alloy, thermal contraction and curvature of a PFM beam were computed for cooling from a heat soak temperature to room temperature. The residual stress distribution in the composite was also computed. Effects of the transformation of the alloy on transient and residual stresses were revealed from the results of the simulations.

Transient stresses developed while cooling from a heat-soak temperature, and residual stresses at ambient temperature, were calculated for the three component composite beam. The transient stresses in the body, opaque and alloy are shown in Figs. 4-(a) to (c), respectively. Transient stresses changed abruptly at the alloy transformation temperature. The thermal contractions of body porcelain and alloy are shown in Fig. 4-(d). Solid lines represent thermal contraction related to the coefficient of thermal expansion and transformation (alloy). Dashed lines are total contraction (thermal contraction and creep relaxation) of the body porcelain surface and the opaque-body porcelain interface. Fig. 4-(e) shows the thermal deflection behavior of porcelainized strip during cooling. Insufficient stress relaxation of porcelain produced initial bending of the composite beam. Transformation strain of the alloy compensated for the strain mismatch between the alloy and the porcelains. After that, the thermal contraction mismatch of the materials also became an important factor in determining the curvature. Fig. 4-(f) shows the residual stress at room temperature.

The major factors which influence the incompatibility stresses within the PFM beam are: (1) the relative coefficients of thermal expansion and (2) the transformation strain and temperature. The effects of these factors were calculated; that is, the transient and residual stresses were simulated when either different coefficients of thermal expansion for the alloy were assumed or when lower transformation temperatures were used. Fig. 5 shows the residual stress in the body porcelain surface and at the opaque-interfaces as a function of alloy coefficient of thermal expansion. Here,

the abscissa represents the coefficient of thermal expansion at room temperature. For these simulations the same transformation temperature (550°C) was assumed. The residual stresses at the surface and the opaque-interface linearly increased in tension and in compression, respectively, as the coefficient of thermal expansion of the alloy increased.

Fig. 6 shows the residual stress in the porcelain surface and in the opaque interface when the transformation temperature changed. Here, the coefficients of thermal expansion were fixed and the transformation temperature was the only variable. The surface and interface of the body porcelain had high tensile and high compressive stresses, respectively, when the transformation temperature was lower than the strain point,  $T_g$ , of the porcelain. The bending deformation at that temperature generated tensile stress in the porcelain surface. Alloy transformations at higher temperatures than the porcelain deformation temperature did not affect the residual stress in the composite beam. Also, the curvature was larger than that for an alloy without a transformation at 600°C, and a coefficient of thermal expansion of  $12 \times 10^{-6}/^{\circ}\text{C}$  at room temperature resulted in a compressive residual stress in the surface of the body porcelain and produced a low curvature of the composite beam (small deformation).

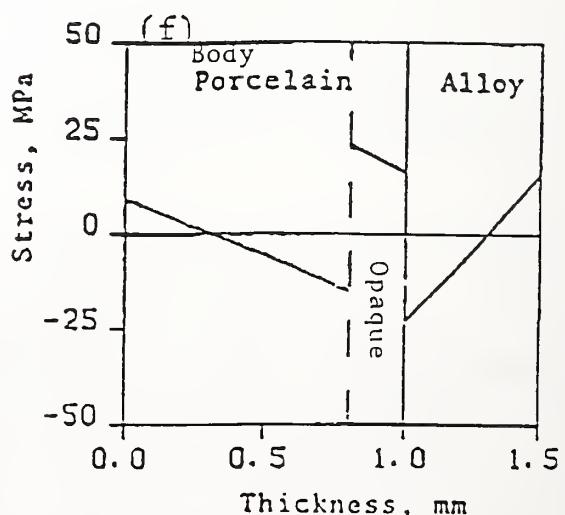
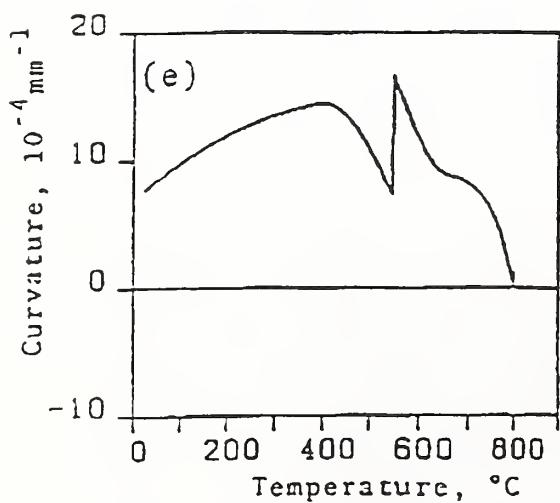
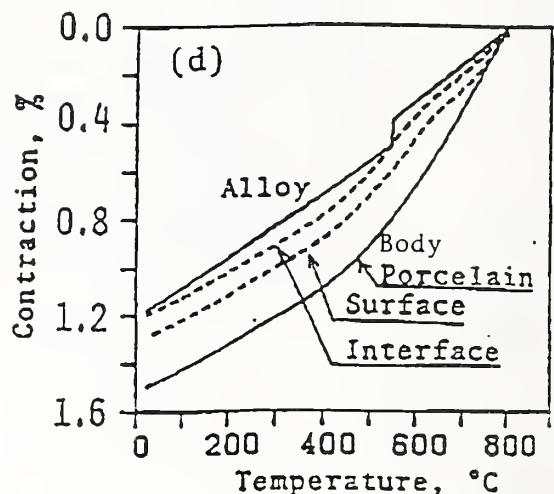
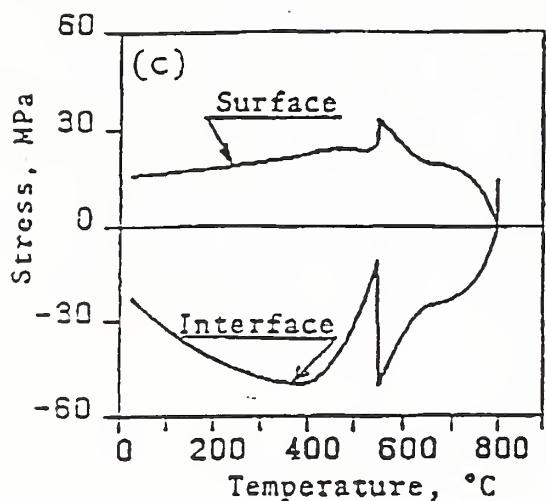
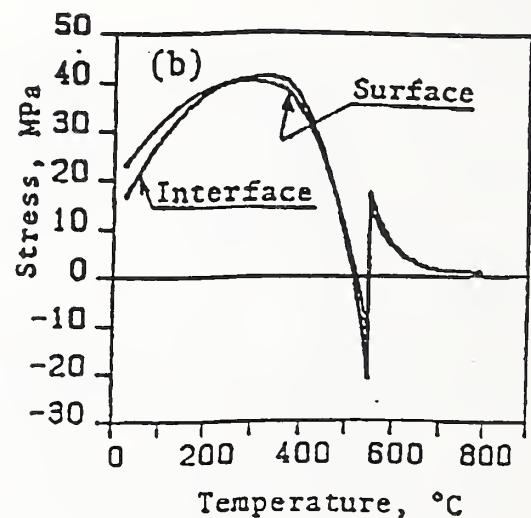
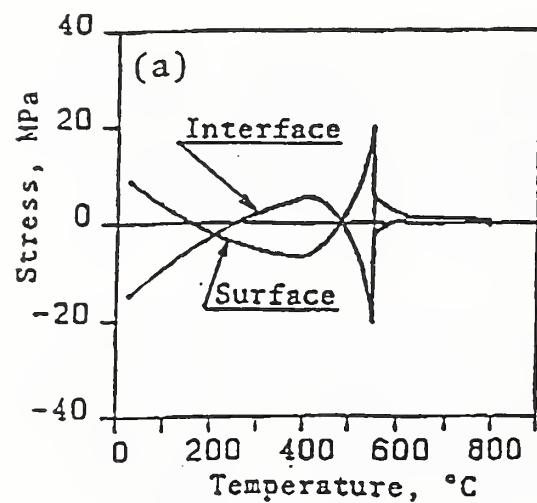


Fig. 4 Transient stresses in PFM strip during cooling from 800°C.  
 (a) Stresses in body porcelain; (b) stresses in opaque porcelain;  
 (c) stresses in alloy. (d) Thermal contraction of body porcelain  
 and alloy during cooling. (e) Curvature of PFM strip during  
 cooling. Here, positive value is bending to porcelain side.  
 (f) Residual stress distribution in PFM strip at room temperature.

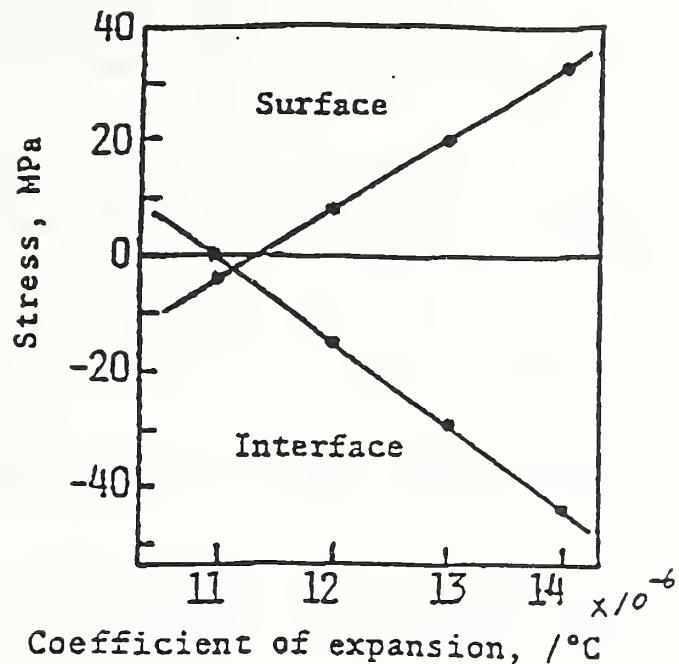


Fig. 5 Relation between residual stresses in body porcelain and coefficient of thermal expansion of alloy.

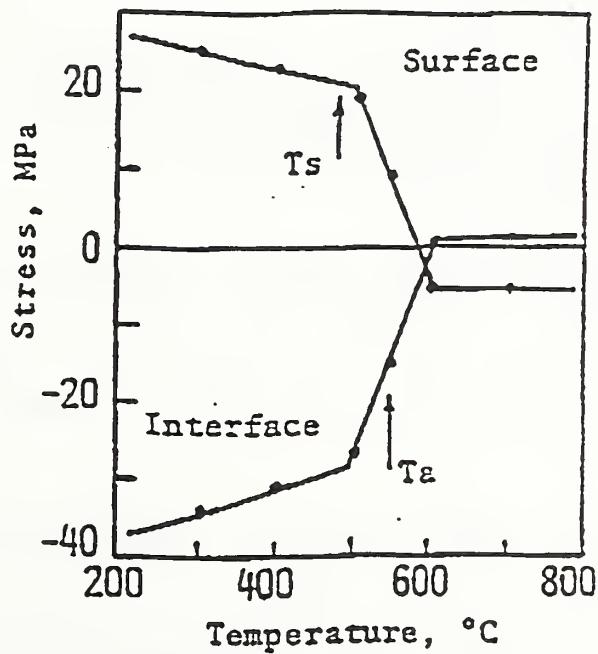


Fig. 6 Relation between residual stresses in body porcelain and temperature of alloy that undergoes a transformation with a decrease in volume between  $\sim 400$  to  $650$  °C.

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Asaoka, K.; Tesk, J.A. Visco-elastic deformation of dental porcelain and porcelain-metal compatibility. *Dental Materials*, 7, 30, 1991.

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Stansbury, J.W. Free radical polymerization of expandable oxaspiro monomers. Book: *Expanding Monomers: Synthesis, Characterization and Applications*, CRC Press, Inc.

### Preprints and Reports

Antonucci, J.M.; Stansbury, J.W.; Cheng, G.W. Synthesis of novel hydrophilic and hydrophobic multifunctional acrylic monomers. IADR Meeting, Acapulco, Mexico.

Tesk, J.A.; Asaoka, K. Effect of transformation of alloy on transient and residual stresses in a porcelain-metal strip. Proc. of 3rd Intl. Conf. on Residual Stress, Tokushima, Japan, July 1991.

Matthews, T.J.; Antonucci, J.M.; de Rijk, W.G. The effect of post cure storage time on diametral tensile strength of composites. IADR Meeting, Acapulco, Mexico.

Schumacher, G.E.; Eichmiller, F.C.; Antonucci, J.M. Effects of surface-active resins on dentin/composite bonds. IADR Meeting, Acapulco, Mexico.

Stansbury, J.W. Improved monomers for double ring-opening polymerization with expansion. Microfilm Proc. of the DMG, IADR Meeting, Acapulco, Mexico.

Tesk, J.A.; Asaoka, K. Residual stress in a porcelain-metal strip related to thermo-physical properties of materials. Proc. of 3rd Intl. Conf. on Residual Stress, Tokushima, Japan, July 1991.

Tesk, J.A.; Antonucci, J.M.; Chiang, M.Y.; de Rijk, W.G.; Keeny, S.M.; McKinney, J.E.; Stansbury, J.W.; Asaoka, K.; Cheng, G.W.; Asaoka, K.; Matthews, T.; Miyazaki, K.; Tang, J. Properties and interactions of oral structures and restorative materials.

Tesk, J.A. Origin of failure in bonded systems. Microfilm Proc. of the DMG, IADR Meeting, Acapulco, Mexico.

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Rusz, J.E.; Antonucci, J.M.; Eichmiller, F.; Anderson, M.H. Adhesive properties of modified glass ionomer cements. J. of Dental Research, in press.

Tesk, J.A. Dental biomaterials and engineering frontiers for the 90's. Proceedings of Third International Kyoto Symposium on Biomaterial Engineering.

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Submitted to Journal or Under Review

Asaoka, K.; Kuwayama, N.; Tesk, J.A. Influence of tempering method on residual stress in dental porcelain, submitted to J. Dent. Res.

Schumacher, G.E.; Eichmiller, F.C.; Antonucci, J.M. Effects of surface-active resins on dentin/composite bonds. IADR Meeting, Acapulco, Mexico, April 1991.

Stansbury, J.W. Synthesis and evaluation of new oxaspiro monomers for double ring-opening polymerization, submitted to J. Dental Research.

Stansbury, J.W. Synthesis and evaluation of novel multifunctional oligomers for dentistry. Submitted to J. Dental Research.

Stansbury, J.W.; Antonucci, J.M. Evaluation of methylene lactone monomers in dental resins, submitted to Dental Materials.

Invited Talks

1. Tesk, J.A. Dental biomaterials and engineering frontiers for the 90's. Kyoto University Research Center, Third International Kyoto Symposium on Biomedical Engineering. Kyoto, Japan, Nov. 20-21, 1990.
2. Tesk, J.A. The advanced technology program: a new model for government/industry innovation. Forsyth Dental Center, Boston MA, March 21-22, 1991.

3. Tesk, J.A. Some areas of focus for dental materials research in the 1990's. Tsrumi University, Yokohama, Japan, Nov. 30, 1990.
4. Tesk, J.A. 1) Origins of failure in bonded systems. 2) and some consideration for biomechanical modeling. Tokushima University Dental School, Tokushima, Japan, August 1, 1991.
5. Antonucci, J.M. Tensile strength of polymeric dental composites as determined by the diametral compression and uniaxial tensile tests. Poster Talk at the 1991 Gordon Research Conference on the Science of Adhesion.

#### Contributed Talks

1. Antonucci, J.M.; Stansbury, J.W.; Cheng, G.W. Synthesis of novel hydrophilic and hydrophobic multifunctional acrylic monomers. IADR Meeting, Acapulco, Mexico, April, 1991.
2. Antonucci, J.M.; Schumacher, G.E.; Eichmiller, F.C. Effects of surface-active resins on dentin/composite bonds. IADR Meeting, Acapulco, Mexico, April, 1991.
3. Antonucci, J.M.; Matthews, T.J.; de Rijk, W.J. The effect of post-cure storage time on diametral tensile strength of composites. IADR Meeting, Acapulco, Mexico, April, 1991.
4. Asaoka, K.; Tesk, J.A. Effect of transformation of alloy on transient and residual stresses in a porcelain-metal strip. Proceedings of the 3rd International Conference on Residual Stress, Tokushima, Japan, July, 1991.
5. Stansbury, J.W. Improved monomers for double ring-opening polymerization with expansion. IADR Meeting, Acapulco, Mexico, April 1991.
6. Tesk, J.A.; Asaoka, K. Residual stress in a porcelain-metal strip related to thermo-physical properties of materials. Proceedings of the 3rd International Conference on Residual Stress, Tokushima, Japan, July, 1991.

Contributed Talks Resulting from Our Collaborative Efforts with the ADA/PRC on a Center of Excellence Materials Science Research Project ("Resin Systems with Minimal Dimensional Changes")

1. Antonucci, J.M.; Stansbury, J.W.; Reed, B.B. Radical reactivity of cyclic acetals. ACS Meeting, NY, NY August, 1991.

2. Antonucci, J.M.; Stansbury, J.W.; Reed, B.B. Radical ring-opening characteristics of cyclic vinyl monomers. ACS Meeting, NY, NY, August, 1991.

Other Interactions or Activities

Joseph M. Antonucci

Member/Consultant of the NIH  
Special Study Section for the Merit  
Review of Small Business Innovative  
(SBIR) Applications

Reviewer for the Journal of Dental  
Research and Dental Materials

John A. Tesk

Editorial Boards: Dental  
Materials; Oral Implantology

Consultant for the National Cancer  
Institute, NIH, Naval Dental School

Reviewer, Journal of Research;  
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## 10. SUPPLEMENTARY NOTES

The research described herein is designed to achieve a number of objectives leading to improved dental restorative materials, techniques and applications of dental materials science for improved delivery of health care. The bulk of the research is related in one manner or another to dental composites, cements, adhesives, and sealants. Composite research focuses on improvements through the development of durable resin matrices, stronger, durable coupling between fillers and resins (defining the best overall combination of components) and optimal curing systems. A major emphasis of the programs the synthesis and applications of monomers which reduce polymerization shrinkage through the use of expanding monomers (or monomers which undergo much less shrinkage than conventional monomers). Research on cements, adhesives and sealants employs many of the same methods as for composites but with further attention to adhesion to dentin and enamel. Analytical techniques include infrared (IR) spectroscopy, chromatography, x-ray analysis, nuclear magnetic resonance, mechanical testing, and shrinkage dilatometry. A new effort involves a pilot study aimed at the use and further development of fluorescent dye spectroscopy for analysis of processes such as curing, applying coupling agents and monitoring the degradation of bonding between fillers and resin matrices. Studies on the wear and durability of dental materials are conducted to complement the generic developmental work on composites, cements, adhesives and sealants. The wear work is to help guide further improvements in materials. A second distinct area of effort focuses on dental alloy and ceramic systems. Weibull statistics and finite element stress analysis are employed for the determination of the strengths of ceramic and ceramic-metal systems as affected by processing parameters and thermo-mechanical properties.

## 12. KEY WORDS (6 TO 12 ENTRIES; ALPHABETICAL ORDER; CAPITALIZE ONLY PROPER NAMES; AND SEPARATE KEY WORDS BY SEMICOLONS)

Dental engineering; dental restorative; dental materials

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